

24938

ASTIA FILE COPY

AERONAUTIC
California Institute

FWD FOR PROCESSING

4-1-288

WILHELM AERONAUTICAL LABORATORY

CALIFORNIA INSTITUTE OF TECHNOLOGY

THERMODYNAMIC FUNCTIONS OF POLYELECTRONIC
ATOMS AT VERY HIGH TEMPERATURES

Robert Vartan Meghreblian

PASADENA, CALIFORNIA

**THERMODYNAMIC FUNCTIONS OF POLYELECTRONIC
ATOMS AT VERY HIGH TEMPERATURES**

**Thesis by
Robert Vartan Meghreblian**

**In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy**

**California Institute of Technology
Pasadena, California**

1953

ACKNOWLEDGEMENTS

The author is indebted to Dr. S. S. Penner for suggesting an investigation to develop useful methods for the calculation of thermodynamic functions at very high temperatures and for help with the formulation and treatment of the physical problems. The author also wishes to express his sincere gratitude to Dr. H. S. Tsien for his interest, encouragement, and extensive help with the analytical development presented in Sections IV and VI.

The introductory section of the thesis was written while the author was holder of a Guggenheim Fellowship in Jet Propulsion. The bulk of the work was done with financial support through the Office of Naval Research under Contract No. Nonr-220(03), NR 015.

The author wishes to express his appreciation to Mrs. B. MacDonald for performing most of the numerical calculations and to Mrs. Elizabeth Fox and Miss Ruth Winkel for typing the thesis.

ABSTRACT

A convergent series representation for the internal partition function of polyelectronic atoms is obtained by assuming a covolume equation of state for the gas as previously applied by Fermi and Urey to the hydrogen atom.

The present investigation is limited to those cases wherein only extranuclear electronic excitation occurs. The contribution of these electronic states to the thermodynamic functions is obtained from an acceptable approximation to the sum of the convergent series for the partition function.

It is shown that at relatively low temperatures (3000°K), the customary method of evaluating the internal partition function (based on the assumption of an ideal gas) agrees to within a few percent with the results obtained from the covolume treatment. However, at higher temperatures the increase in size of the excited atoms, along with the appearance of charged particles produced by ionization, render the ideal gas treatment inadequate. Since the interaction potentials of charged particles are not known in general, an approximate procedure, which neglects these interactions, is suggested for analyzing a system wherein ions and free electrons constitute a small fraction of the total population. This procedure should be useful for treating gaseous mixtures to temperatures of about $10,000^{\circ}\text{K}$.

TABLE OF CONTENTS

Acknowledgement	i
Abstract	ii
Table of Contents	iii
Table of Figures	v
Symbols	vi
I. INTRODUCTION AND SUMMARY	1
II. THERMODYNAMIC DERIVATION OF A GENERAL EXPRESSION FOR THE PARTITION FUNCTION	5
A. Covolume Equation of State	
B. Total Partition Function	
III. QUANTUM STATES FOR POLYELECTRONIC ATOMS	14
A. Excited Electronic States	14
B. Hydrogen-like Approximation for Higher Elec- tronic States	15
C. Ionization and Multiple Excitation of Polyelec- tronic Atoms	18
IV. CALCULATION OF THERMODYNAMIC FUNCTIONS	23
A. Evaluation of Weighting Function	23
B. Internal Partition Function	29
V. ATOMIC VOLUMES	37
A. Hydrogen-like Model	37
B. Calculation of Atomic Volumes	42
VI. APPLICATION OF METHOD	44
A. Fundamental Relations	44
B. Thermodynamic Functions	44
C. Equation of State	46
D. Discussion	49

REFERENCES

APPENDIX

- A. Classical Solution Thermodynamics**
- B. Computation of $\overline{r^3}$ for Hydrogen**
- C. Some Useful Formulae for Iteration Procedure**

LIST OF FIGURES

1. Isoelectronic Sequences for Nitrogen I Configuration
2. The Function $h(n)$
3. The Function $q(n)$
4. The Functions μ , δ and τ
5. The Function γ_{ln}
6. Selection of γ_0
7. Equation of State for Lithium I at 20 atm. (high temperature range)
8. Equation of State for Lithium I at 20 atm. (low temperature range)
9. Equation of State for Nitrogen I at 20 atm.
10. Thermodynamic Functions of Lithium I at 1 atm.
11. Thermodynamic Functions of Lithium I at 20 atm.
12. Thermodynamic Functions of Lithium I at 100 atm.

SYMBOLS

a_1	first Bohr radius
b	covolume correction
b_i	atomic volume of species i
b_{ij}	effective collision volume of atoms of species i and j
b_m	average effective collision volume for mixture
c	velocity of light
C	heat capacity
d	reference to d -state of excited electron
f	reference to f -state of excited electron
F	Gibb's free energy
g	statistical weight
h	Planck's constant
h_i	enthalpy per atom of species i
H	enthalpy of mixture
k	Boltzmann's constant
K	equilibrium constant of chemical reaction
l	azimuthal quantum number
L	quantum number measuring the total angular momentum vector of an atom
m	mass
n	principal quantum number
N	number of particles
n	number of particles at chemical equilibrium
p	reference to p -state of excited electron
P	pressure

q	internal partition function divided by $e^{-W_i/kT}$
Q	partition function
r	radius
R_∞	Rydberg constant
Δ	entropy per atom or reference to Δ -state of excited electron
S	entropy of mixture, Slater's shielding constant or spin quantum number
T	temperature
V	volume
W_i	term value of quantum state i
x_i	mole fraction of species i
X	chemical symbol
Z	atomic number
Z_{eff}	effective core charge
α, β	state parameters
ϵ_i	internal energy per atom of species i
ϑ	angular coordinate
μ_i	chemical potential per atom of species i
σ	collision diameter
φ	angular coordinate
Ψ	wave function
w_i	excitation energy for quantum state i

Subscripts

c	reference to atomic core
i, j	internal energy states
int	reference to internal energy states

l reference to azimuthal quantum number

n reference to principal quantum number

trans reference to translational energy

Superscripts

\circ reference to the pure state of a given species

I. INTRODUCTION AND SUMMARY

If the temperature of an atomic gas is sufficiently high to produce appreciable equilibrium concentrations of atoms in excited energy states, then an accurate calculation of the thermodynamic functions of the system, including contributions from these higher energy states, becomes difficult because of the apparent divergence of the partition function. Practical examples of high temperature systems of this type are encountered in researches on stellar atmospheres and in shock waves. This problem is also of interest in connection with the application of high-performance propellants and nuclear energy sources to jet propulsion devices.

It has been known for some time that the internal partition functions of ideal monatomic gases diverge if all of the possible energy states are included. The terms of the infinite series which define the partition function consist of the product of the statistical weight and of an exponential factor involving the negative of the excitation energy of each quantum state divided by kT . This exponential factor for the higher states approaches a finite limit, whereas the statistical weight increases indefinitely. Thus although the first few terms of the partition function may appear to be converging, the higher terms gradually increase and become arbitrarily large. The series therefore diverges. However, it is known that at relatively low temperatures, the first few terms of this series yield a good approximation to the internal partition function.

The principal results obtained in the present analysis are:

- (a) a convergent representation is obtained for the partition function of polyelectronic atoms; (b) relations for the thermodynamic functions

of un-ionized gases at very high temperatures are derived from this expression; and (c) the limit of validity of the customary procedure is determined by comparing results for the thermodynamic functions based on that method with the results obtained from the convergent series. The convergent series representation of the internal partition function for all atoms is obtained by selecting a covolume equation of state for the gaseous mixture. This procedure was used previously by Fermi⁽¹⁾ and Urey⁽²⁾ in their investigations on the hydrogen atom. Computations based on the present method show that the covolume correction is the major deviation from ideal gas behavior for gaseous mixtures at relatively low temperatures (3000°K) at moderate and at elevated pressures. However, it is found that this correction is small, and that the convergent solution to the partition function yields results which agree to within a few percent with the results obtained for an ideal gas. Thus it would appear that the customary procedure for computing internal partition functions at low temperatures is entirely adequate for engineering calculations. At higher temperatures ions and free electrons appear in appreciable concentrations, and proper account must be taken of the increase in the number of particles although the interaction of charged particles in the mixture can be neglected in first approximation*. By applying the present method, one can determine the relative importance of the covolume and ionization corrections. Sample calculations for hydrogen, lithium and nitrogen show that at temperatures above about 7000°K ionization can not be neglected even at pressures as high as 20 atmos.

* This effect may be accounted for by using, for example, the Debye-Hückel theory as applied by Williamson in the case of hydrogen.
Cf. Astrophysical J. 103 139 (1946).

The procedure developed for the calculation of thermodynamic functions of neutral atoms remains valid, in principle, even under conditions in which appreciable ionization occurs. However, before applications can be made to real systems, it will be necessary to investigate in some detail (a) small perturbations of the calculations for neutral atoms and (b) interaction terms corresponding to binary collisions between neutral atoms and charged particles. But, these calculations are extremely difficult to carry out, because the interaction potentials of charged particles are generally not known.

It is expected that these interaction terms will yield small corrections on the thermodynamic functions of systems wherein ionization is of the order of 10 percent (temperatures at about $10,000^{\circ}\text{K}$). Consequently, a first approximation to these functions may be obtained by treating the system with the methods of classical solution thermodynamics and neglecting the interaction between the neutral atoms and the charged particles. The present method may be utilized to compute the thermodynamic functions of the neutral atoms, and the contributions of the ions and free electrons may be calculated by using, for example, the Debye-Hückel theory.

The problem of evaluating partition functions may be attacked by using either the methods of statistical mechanics or the methods of thermodynamics. The former approach was applied by R. H. Fowler⁽³⁾ and by Planck* to the investigation of stellar atmospheres. The latter approach was applied by Fermi⁽¹⁾ and by Urey⁽²⁾. The advantages of the statistical methods can be utilized only if a realistic description of the interaction potentials for atoms in their ground states and in

*Cf. Reference 3, p. 353.

excited electronic states can be given. Since these interaction potentials are generally not known, the statistical methods offer no obvious advantages over the simpler thermodynamic methods, which involve the implicit assumptions that the atoms are rigid elastic spheres interacting according to a square-well potential profile.

The present study utilizes the methods of statistical thermodynamics for the evaluation of internal partition functions for atomic gases distributed at equilibrium in the accessible electronic energy states. It is assumed that the presence of atoms in excited energy states leads to non-ideal gas behavior only insofar as a covolume correction is required to the equation of state. As is to be expected from the use of a covolume correction, the necessary weighting function to provide convergence of the series defining the internal partition function is dependent upon the effective atomic volumes of the excited electronic states. This conclusion was also stated by Urey and by Fermi. It is shown in the present studies that the exact expression for the weighting function can be obtained along with the solution for the total partition function. The reduction of the present solution to the classical value of the partition function for an ideal gas is readily demonstrated.

Assuming the validity of a covolume equation of state, it is clear that the calculation of the thermodynamic properties of gaseous systems depends upon the evaluation of the weighting function. It is found that the weighting function is determined by the solution of three simultaneous transcendental equations wherein the unknowns are dependent upon the quantum energy levels and upon the thermodynamic parameters of state, viz., the pressure and temperature.

A solution to the set of simultaneous equations is obtained by introducing a closed form expression for the internal partition function.

The dependence of the weighting function on the atomic volumes has been indicated. Two methods for estimating these volumes are investigated. The first, an approximate technique, is the method of screening constants; the second uses empirical wave functions obtained by the method of Hartree^(4,5) from known energy levels. The latter, although more reliable, is extremely laborious. It is shown by means of actual calculations on the potassium atom, that the screening constant treatment yields atomic volumes which are in good agreement with those obtained by the Hartree method, especially for the higher energy states. For these states, the effective core charge reduces to one so that an atom acquires essentially a hydrogen-like structure. It is believed that the application of the screening constant method to the lower energy states, and the use of the hydrogen-like approximation for the higher states, provides a useful technique for evaluating atomic volumes.

Application of the proposed method to the determination of the thermodynamic functions of pure atomic gases at high temperature is illustrated by sample calculations on the un-ionized lithium atom. The calculations have been performed for pressures from 1 atm. to 100 atm., and for temperatures between 5000°K and 20,000°K. The results obtained for 100 atm. pressure are compared with the classical solution, and it is found that in the temperature range wherein ionization is small the ideal gas results differ by a few percent from the results based on a covolume equation of state.

II. THERMODYNAMIC DERIVATION OF A GENERAL EXPRESSION FOR THE PARTITION FUNCTION

A. Covolume Equation of State

At high temperatures appreciable numbers of atoms will occupy higher energy states for which effective atomic volumes are no longer negligibly small; hence, the need for a covolume correction to the equation of state. It is apparent that the atomic volumes increase with increasing energy levels. Thus, the available free space in the gas is decreased thereby increasing the probability for collision. Several investigators have examined the problem of collisions between rigid elastic spheres, and it is agreed that on the basis of such a model, the covolume correction b is proportional to the average effective volume b_m of a binary collision (the gas densities of interest here are too low to yield appreciable probabilities for collisions involving more than two atoms). First order calculations for the proportionality factor indicate $\frac{N}{2}$ to be the correct value⁽⁷⁾. In this case N is the total number of atoms present in the mixture of total volume V , pressure P and temperature T . The corresponding equation of state is

$$P(V-b) = P(V - \frac{N}{2}b_m) = NkT \quad (1)$$

Following Fermi⁽¹⁾ and Urey⁽²⁾ we consider a system which consists of only one chemical component and regard the various excited electronic states of the atom as separate species. The resulting system is composed, therefore, of a mixture of gases of the same atomic weight. Of the N atoms present in this mixture, N_i will occupy the internal energy state ω_i . Evidently

$$\sum_i N_i = N \quad (2)$$

The average effective collision volume b_m may be evaluated in terms of the individual atomic volumes. Consider therefore the collision of an atom of species i with one of species j . If we denote by r_i and r_j the radii of these atoms, then the effective collision radius σ_{ij} for rigid elastic spheres is

$$\begin{aligned} \sigma_{ij} &= r_i + r_j \\ &= \left(\frac{3}{4\pi}\right)^{\frac{1}{3}} (b_i^{\frac{1}{3}} + b_j^{\frac{1}{3}}) \end{aligned}$$

where b_i, b_j = volume of atom of type i, j . The effective collision volume b_{ij} is equal to that of a sphere of radius σ_{ij} . Thus

$$b_{ij} = \frac{4\pi}{3} (\sigma_{ij})^3 = (b_i^{\frac{1}{3}} + b_j^{\frac{1}{3}})^3$$

An average effective collision volume b_m for the system may be defined by

$$b_m = \frac{\sum_{i,j} (\text{total number of collisions}) \times (\text{corresponding collision volume})}{\sum_{i,j} (\text{total number of collisions})}$$

The total number of collisions between atoms of types i and j is given by the number of combinations of N_i and N_j things taken two at a time such that one of each is present in every set. Thus the total number of collisions is

$$\begin{aligned} &\sum_{i,j} N_i N_j \\ \text{and} \quad b_m &= \frac{\sum_{i,j} N_i N_j (b_i^{\frac{1}{3}} + b_j^{\frac{1}{3}})^3}{\sum_{i,j} N_i N_j} \end{aligned}$$

But from Equation (2), $\sum_i N_i = N$; therefore, $\sum_{i,j} N_i N_j = N^2$ and

$$b_m = \frac{1}{N^2} \sum_{i,j} N_i N_j (b_i^{\frac{1}{3}} + b_j^{\frac{1}{3}})^3 \quad (3)$$

Hence the covolume correction b in terms of the atomic volume is

$$b = \frac{1}{2N} \sum_{i,j} N_i N_j (b_i^{\frac{1}{3}} + b_j^{\frac{1}{3}})^3 \quad (4)$$

This result was indicated by Fermi,⁽¹⁾ but without proof.

The generalized expression for the covolume correction b based on a two-body collision mechanism is reexamined in Sec. VI C in greater detail. A second relation, more suitable for equation of state calculations, is readily obtained from this form.

B. The Total Partition Function

It is the purpose of the present section to derive an expression for the total partition function of a gaseous system of chemically identical atoms occupying various electronic energy states by using the methods of classical solution thermodynamics^(8,9) (cf. Appendix A). Statistical relations will be used only to assist in identifying and simplifying the results. The final expression for the partition function of imperfect gases is shown to be of familiar form, differing from the classical solutions only through an additional factor which represents a covolume correction. Furthermore, this correction factor is, in zeroth approximation, identical with the result of Fermi, and is also of the same form as the correction factor obtained by Urey for a mixture of hydrogen atoms obeying the covolume equation of state.

An expression for the total partition function can be derived from the definition of the chemical potential. Let us consider the chemical potential μ_i for an atom of species i in a gaseous mixture composed of atoms which are in different energy levels. Then (Cf. Appendix A),

$$\mu_i = \mu_i^\circ + kT \ln \frac{N_i}{N} \quad (\text{A-3})$$

where μ_i° is the chemical potential of i in the pure state, k represents the Boltzmann constant and $\frac{N_i}{N}$ is evidently the mole fraction of i . If h_i° and Δ_i° denote the enthalpy and entropy per atom of pure component i at P and T in a volume V_i° occupied by N_i atoms, then we may write

$$\mu_i^\circ = h_i^\circ - T\Delta_i^\circ \quad (5)$$

Note that the superscript \circ denotes a pure component.

The total energy per atom ϵ_i° may be separated, in good approximation, into translational and internal components. Thus

$$\epsilon_i^\circ = \frac{3}{2}kT + w_i \quad (6)$$

The enthalpy for N_i atoms of species i in the pure state at pressure P , temperature T , and volume V_i° is

$$H_i^\circ = E_i^\circ + PV_i^\circ$$

Hence, the enthalpy per atom is

$$h_i^\circ \equiv \frac{H_i^\circ}{N_i} = \epsilon_i^\circ + \frac{PV_i^\circ}{N_i} \quad (7)$$

where the total internal energy E is

$$E = \sum_i E_i^\circ = \sum_i N_i \epsilon_i^\circ \quad (\text{A-21})$$

and the total volume is given by

$$V = \sum_i V_i^\circ \quad (\text{A-17})$$

Substitution of Equations (2), (4) and (A-17) into (1) yields

$$\sum_i \left\{ P V_i^\circ - \frac{P N_i}{2N} \sum_j N_j (b_i^{\frac{1}{3}} + b_j^{\frac{1}{3}})^3 - N_i kT \right\} = 0$$

This equation must hold for a system containing any arbitrary number of atoms. The only physically acceptable solution is

$$\frac{P V_i^\circ}{N_i} = \frac{P}{2N} \sum_j N_j (b_i^{\frac{1}{3}} + b_j^{\frac{1}{3}})^3 + kT \quad (8)$$

It is evident from Equation (4) that

$$\frac{1}{2N} \sum_j N_j (b_i^{\frac{1}{3}} + b_j^{\frac{1}{3}})^3 = \frac{\partial b}{\partial N_i} \quad (9)$$

If Equations (8) and (9) are used in Equation (7) along with Equation (6), then

$$h_i^\circ = \frac{5}{2} kT + w_i + P \frac{\partial b}{\partial N_i}$$

Hence, from Equation (5),

$$\mu_i^\circ = \frac{5}{2} kT + w_i + P \frac{\partial b}{\partial N_i} - T \Delta_i^\circ$$

and from Equation (A-3)

$$\ln \frac{N_i}{N} = -\frac{5}{2} + \frac{\mu_i}{kT} - \frac{w_i}{kT} - \frac{P}{kT} \frac{\partial b}{\partial N_i} + \frac{\Delta_i^\circ}{k}$$

At equilibrium $\mu_i = \mu = \text{constant}$. Therefore, solving for N_i and summing over all states, we obtain

$$\sum_i N_i = N = (N e^{-\frac{s}{2}}) e^{\mu/kT} \sum_i e^{\Delta_i^{\circ}/k} e^{-w_i/kT} e^{-\frac{P}{kT} \frac{\partial b}{\partial N_i}}$$

If we define the total partition function Q in the usual way, (10, 11)

$$Q \equiv N e^{-\mu/kT} \quad (10)$$

then

$$Q = (N e^{-\frac{s}{2}}) \sum_i e^{\Delta_i^{\circ}/k} e^{-w_i/kT - \theta_i} \quad (11)$$

where the weighting function $e^{-\theta_i}$ has been introduced, and

$$\theta_i \equiv \frac{P}{kT} \frac{\partial b}{\partial N_i} \quad (12)$$

For ideal gases θ_i is evidently equal to zero. Since the factor $\frac{\partial b}{\partial N_i}$ increases rapidly with increasing energy level, $e^{-\theta_i}$ will cause a rapid decrease of the numerical values of the terms of the summation as w_i is increased.

The entropy per atom Δ_i° may be separated, in good approximation, into a translational and an internal component. Thus

$$\Delta_i^{\circ} = (\Delta_i^{\circ})_{\text{trans}} + (\Delta_i^{\circ})_{\text{int}} \quad (13)$$

The translational component $(\Delta_i^{\circ})_{\text{trans}}$ is independent of the internal energy states w_i . It is given by the Sackur-Tetrode relation. (12)

For an imperfect gas, the appropriate expression for the translational entropy per atom is

$$(\Delta_i^{\circ})_{\text{trans}} = \Delta_{\text{trans}} = k \ln \left[\frac{(2\pi m k T)^{\frac{3}{2}} e^{\frac{s}{2}} (V-b)}{N h^3} \right] \quad (14)$$

where m is the mass per particle and h represents Planck's constant. The contribution to Δ_i° from the internal energy states $(\Delta_i^\circ)_{int}$ may be evaluated by means of the following argument: It is known from statistical mechanics that $(\Delta_i^\circ)_{int}$ may be defined by the relation *

$$(\Delta_i^\circ)_{int} \equiv k \ln w \quad (15)$$

where w denotes the number of quantum states available to the system. In the case of a system consisting of the pure component i which has available to it only one quantum state w_i , w is evidently the statistical weight g_i (degeneracy) of that quantum state; hence,

$$(\Delta_i^\circ)_{int} = k \ln g_i \quad (16)$$

and it follows from Equations (13) to (16) that

$$e^{\Delta_i^\circ/k} = \frac{(2\pi m k T)^{\frac{3}{2}} e^{\frac{5}{2}(V-b)} g_i}{N h^3} \quad (17)$$

Substitution of Equation (17) into Equation (11) yields

$$Q = \frac{(2\pi m k T)^{\frac{3}{2}} (V-b)}{h^3} \sum_i g_i e^{-w_i/kT - \theta_i} \quad (18)$$

where the factor before the summation sign evidently represents the translational partition function for a gas obeying the covolume equation of state. One can readily identify the complete expression (18) with the familiar approximation

$$Q = Q_{trans} \cdot Q_{int} \quad (19)$$

* Cf. Ref. 10, p. 92.

where

$$Q_{trans} = \frac{(2\pi mkT)^{\frac{3}{2}} (V-b)}{h^3} \quad (20)$$

and

$$Q_{int} = \sum_i g_i e^{-\omega_i/kT - \theta_i} \quad (21)$$

The expression for the internal partition function Q_{int} is of the usual form except for the factor $e^{-\theta_i}$ which appears as a direct consequence of the covolume correction introduced into the equation of state. It is of interest to note that as $b, \frac{\partial b}{\partial N_i} \rightarrow 0$, Equation (21) reduces to the total partition function of a perfect gas:

$$Q_{\infty} = \frac{(2\pi mkT)^{\frac{3}{2}} V}{h^3} \sum_i g_i e^{-\omega_i/kT}$$

It is well known that this expression diverges if enough terms are considered in the summation. The customary practice has been to compute Q_{int} by using only the first few terms of this relation and to assume that the higher energy states make negligible contributions. At low temperatures this procedure yields acceptable results. For these cases the comparison of results obtained from such an approximation with the correct values obtained from Equation (21) shows agreement to within one percent. It is of interest to note that for temperatures in the order of 5000°K, the first term alone from either of the above expressions for Q_{int} yields results which are accurate to within a few percent.

The functional form of the covolume correction given in Equation (12) is identical with the relation obtained previously by Fermi⁽¹⁾ as the result of a less complete analysis than has been given here. It is evident from Equation (20) that a covolume correction occurs

also in the expression for the translational partition function. However, this term is of no consequence as regards the calculation of internal partition functions. Equation (21) will be referred to hereafter as Fermi's equation for the internal partition function of a gas mixture obeying the covolume equation of state or, more briefly, as Fermi's equation. It will serve as the basic relation for the determination of thermodynamic functions of atomic gases at elevated temperatures.

III. QUANTUM STATES FOR POLYELECTRONIC ATOMS

A. Excited Electronic States

The internal partition function as given by the Fermi Equation is defined as a infinite series which extends over all internal states i , beginning with the ground state $i = 1$. Each of these states i denotes a distinct quantum state of the atom. In the present analysis we shall confine our attention to a consideration of the states of the extra-nuclear electrons, and shall neglect the quantum states of the nucleus. The rotational and vibrational excitation energies of the nucleus, even for the heaviest elements, ⁽¹³⁾ are known to be at least of the order of 10^4 e. v. These energies are several orders of magnitude larger than the highest degree of extranuclear excitation which can be expected at the temperatures of interest. At most we shall be concerned with the first few ionization stages of the atom. Consequently, the index i is used to represent the excited electronic states of the atom and, in fact, may be replaced by an appropriate set of quantum numbers. Thus

$$i = i(n, L, S)$$

where n is the principal quantum number, L the quantum number measuring the total angular momentum vector for the atom, and S , the spin quantum number for the atom.

The excitation energies w_i are given in the usual way, viz.,

$$w_i \equiv W_i - W_1$$

Here W_i denotes the term value for state i and W_1 refers to the ground state. These data are readily available from spectroscopic measurements (e. g. Landolt - Bornstein "Tabellen"). An accurate

calculation of Q_{int} requires a complete compilation of these term values. Although there exist infinitely many term values, the usual practice in tabulating these data is to list the values W_i up to perhaps $n = 10$. For temperatures below 3000°K , it has been customary to compute Q_{int} by utilizing only the first few terms in Equation (21). At higher temperatures, it is necessary to take more terms.

B. Hydrogen-Like Approximation for Higher Electronic States

It has been noted that the higher electronic term values may not have been determined experimentally; nevertheless, it is possible to predict these term values by assuming a hydrogen-like atomic configuration. This approximation can be justified on the basis of simple physical arguments. As the excited electron occupies higher energy states, the net effect of the core structure (the nucleus and remaining electrons) on this electron is much like the effect of the hydrogen nucleus on its electron. The inner electrons shield the excited electron from the full strength of the nuclear field. In fact, as the atom approaches the ionized state, the effective core charge approaches 1, and the structure becomes hydrogen-like. In practice this limiting condition is assumed to exist much earlier. Consequently, one can estimate approximately the remaining term values by using the well-known Bohr hydrogen model.

It appears appropriate, therefore, to separate the internal partition function into two parts. The first part, a finite sum, accounts for the contribution of the known, spectroscopically determined, term values. For low temperatures this part makes the major contribution to Q_{int} . The remaining portion of the internal partition function is determined by a hydrogen-like approximation, and is represented by an infinite series; thus

$$Q_{int} = e^{-W_i/kT} \left\{ \sum_{i=1}^{\lambda} g_i e^{W_i/kT - \theta_i} + \sum_{i=\lambda+1}^{\infty} g_i e^{W_i/kT - \theta_i} \right\} \quad (22)$$

The separation is made at some value of $i=\lambda$ such that W_i is dependent, in first approximation, only on the principal quantum number n , that is to say, it is assumed that for given n , the term values differ by negligible amounts for the allowed values of L and S .

This assumption is well substantiated by the spectroscopic data. An inspection of these data shows that for a particular atom, there exists some value of $n=\alpha$, beyond which the L and S variations in the term values may be neglected. It follows therefore that for $i > \lambda$

$$W_i \sim W_n$$

In accordance with the hydrogen-like approximation, the index i will be replaced by the pair n and l , the principal and azimuthal quantum numbers respectively. Thus

$$i \rightarrow i(n, l)$$

The infinite series in Equation (22) may now be written as

$$\sum_{n=\alpha}^{\infty} \sum_{l=0}^{n-1} g_{nl} e^{W_{nl}/kT - \theta_{nl}} \equiv \sum_{n,l} q_{nl} \quad (23)$$

The summation over i is replaced by the double sum over n and l . Although the description of the energy states by the quantum numbers (n, l) is a customary one, the above formulation is primarily a formalism. Note that for given n , the summation over the allowed values of l is required first; the summation over n is carried out last.

This procedure has no particular physical significance and has been adopted only because it is convenient. The correct order of the absolute magnitudes of the energy states is known to be *

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 6s \dots$$

The procedure indicated in Equation (23) may be used, because the series is absolutely convergent.

If the hydrogen-like approximation is applied to the calculation of θ_{ln} and g_{ln} , then one can readily compute appropriate expressions for each. The statistical weight g_{ln} for a hydrogen-like configuration is given by the product of the statistical weight of the core and the weights for the single excited electron. If we denote the core degeneracy by g_c , and note that the degeneracy of a single electron for all values of l for given n is $2(2l + 1)$, then we find that the statistical weight for a given state w_{ln} is

$$g_{ln} = 2g_c(2l+1) \quad (24)$$

The term values W_{ln} for a hydrogen-like configuration are given by

$$W_{ln} \simeq \frac{R_0 hc}{n^2} \quad (25)$$

where R_0 is the Rydberg constant (13.53 e.v.), and c is the velocity of light. The substitution of Equations (24) and (25) into the series (23) yields

$$\sum_{n,l} g_{ln} = 2g_c \sum_{n=a}^{\infty} e^{\alpha/n^2} \sum_{l=0}^{n-1} (2l+1) e^{-\theta_{ln}}$$

* Cf. Pauling, L., "The Nature of the Chemical Bond", Cornell University Press, Ithaca, 2nd Edition 1940.

The state parameter α is equal to $R_0 hc/kT$.

The internal partition function may be given now in terms of n and l :

$$Q_{int} = e^{-W_i/kT} \left\{ \sum_{i=1}^{\lambda} q_i + 2g_c \sum_{n=a}^{\infty} e^{\alpha/n^2} \sum_{l=0}^{n-1} (2l+1) e^{-\theta_{nl}} \right\} \quad (26)$$

where

$$q_i \equiv g_i e^{W_i/kT - \theta_i} \quad (27)$$

C. Ionization and Multiple Excitation of Polyelectronic Atoms

The present study is limited to a consideration of gaseous systems at temperatures and pressures for which the chemical species present will occupy, in appreciable numbers, only the electronic states of the neutral atom. A system of this kind is encountered in several engineering problems which are of current interest, viz., high-performance rocket devices and very strong shock waves. Important exceptions occur in problems of stellar atmospheres where extensive ionization is present. In the outer regions of the stars (chromosphere) the pressures are of the order of 10^{-6} atmospheres, and under these conditions the constituent elements of the atmosphere (e. g. Ca, Ba, Sr, Si, He. . . .) appear in the first and higher stages of ionization. Although the present analysis is derived for systems which contain only neutral particles, it is evident that similar treatments can be developed for mixtures of atoms, ions and free electrons. However, the results which we obtain are useful for the description of the un-ionized atoms even in mixtures which contain charged particles. If the ions and electrons constitute a small fraction of the total population, then one can

obtain an approximate treatment by neglecting their interaction with the neutral atoms.

The applicability of the present method to a specific problem depends on the degree of ionization which occurs in the system, and the proposed procedure is valid as long as the number of ionized atoms represent only a few percent of the total population. The degree of ionization for a particular component in a mixture is independent of the other elements present. Thus we may confine our attention to a single reaction, which may be represented by the equation



X is the chemical symbol of the neutral element and e represents the electron freed in the ionization process. It was pointed out by Saha⁽¹⁴⁾ that this reaction could be treated by standard thermodynamic methods; therefore, the concept of an equilibrium constant is applicable. Let

$$\begin{aligned} N_0 &= N - N_1 & \Delta N &= 1 \\ N_1 &= N_e & \eta &= N + N_1 \end{aligned} \quad (29)$$

where ΔN denotes the net increase in the number of particles produced by ionization as shown by Equation (28), and η the total number of particles present at equilibrium. N represents the initial number of atoms of X , N_0 the number of neutral atoms at equilibrium, N_1 the number of ionized atoms, and N_e the number of electrons. The

equilibrium constants are related by

$$K_p = K_N \left(\frac{P}{\eta} \right)^{\Delta N}$$

and $K_N = N_i N_e / N_o$. Evidently

$$K_p = \frac{P N_i^2}{N^2 - N_i^2}$$

If we denote $x_i \equiv N_i / N$, then

$$x_i = \left(\frac{K_p / P}{1 + K_p / P} \right)^{\frac{1}{2}} \quad x_o = 1 - x_i \quad (30)$$

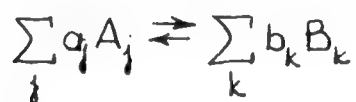
Therefore, the degree of ionization is

$$\frac{N_i}{N_o} = \frac{x_i}{1 - x_i} \quad (31)$$

The equilibrium constant K_p is obtained readily from the familiar expression

$$K_p = P \exp \left\{ -\frac{1}{KT} \left[\sum_k b_k F_{B_k}^\circ - \sum_j a_j F_{A_j}^\circ \right] \right\}$$

which corresponds to the reaction



and

$$\sum_k b_k F_{B_k}^\circ - \sum_j a_j F_{A_j}^\circ \equiv \Delta F^\circ = \Delta H^\circ - T \Delta S^\circ$$

The quantity $F_{A_j}^\circ$ denotes the Gibbs free energy of the pure component A_j at T and P , and is related to the free energy F_{A_j} of A_j in the mixture by an expression analogous to (1-3). Note that this formulation differs from the customary one in that the standard properties are those

of the pure component A_j at T and P rather than the properties of A_j in the mixture measured at standard temperature and pressure. If one expands the expression for ΔF° , noting that the individual atoms have both translational and electronic degrees of freedom, then one obtains the well-known Saha equation:⁽¹⁵⁾

$$K_p = 2 \frac{(Q_{int})_1}{(Q_{int})_0} \left(\frac{2\pi m_e kT}{h^2} \right)^{\frac{3}{2}} kT e^{-W_1/kT} \quad (32)$$

Here m_e denotes the mass of the electron, W_1 is the ionization potential for reaction (26), and $(Q_{int})_j$ is the internal partition function for the j -fold ionized atom. The substitution of this expression for K_p into Equations (30) and (31) yields the ratio $\frac{N_1}{N_0}$. Unsöld* has constructed a nomogram, which simplifies numerical computations appreciably.

When collecting the spectroscopic data for the evaluation of the finite sum in Equation (26), it is important to note that the tabulated data will necessarily include only observed transitions. In the case of an equilibrium process (which is of interest in the present analysis) all energy states are available to the system. Accordingly, one must calculate term values which are not observed spectroscopically. Furthermore, multiple excitations (the simultaneous excitation of two or more electrons) may occur. An accurate computation must, of course, make allowance for all of these possibilities. Although the available states can be predicted on the basis of the possible electronic configurations by well-known procedures,⁽¹⁶⁾ the corres-

*Cf. Reference 15, pp. 66-74.

ponding term values are somewhat more difficult to specify. The method of isoelectronic sequences⁽¹⁷⁾ may be useful in this connection. The term values of unobserved states for a given atom may be predicted by examining the corresponding states of other atoms which have the same electronic configuration. Because of similar electronic configurations, the same states are assumed to be accessible to each atom. The only difference between these various atoms will be the magnitudes of the transition energies (term values) because of the different nuclear charges. In the present analysis it was found convenient to plot the transition energies of the state in question as a function of the effective atomic number Z_{eff} . Illustrative plots for the nitrogen I configuration, states $^2S_{1/2}(1d^2, 2d^2 2p^2, 3d)$ and $^2D(1d^2, 2d 2p^4)$, are presented in Figure 1. Evidently one or two points are adequate for establishing a given curve. This result is produced by the fact that the transition energy is proportional to the square of the effective field strength.

IV. CALCULATION OF THERMODYNAMIC FUNCTIONS

A. Evaluation of Weighting Function

The derivation of the weighting function presented in Section II showed the dependence of $e^{-\theta_i}$ on the derivative $\frac{\partial b}{\partial N_i}$. The definition of this derivative as given by Equation (9) may be simplified by introducing the Boltzmann relation,

$$N_j = \frac{N_i g_j}{g_i} e^{-w_j/kT - \theta_j + \theta_i} \quad (33)$$

In addition let us assume that the atomic volumes b_j are given by the following relation (γ_0 , α_0 and v_j are defined in V A):

$$b_j = \left(\frac{4\alpha_0^3 \pi \gamma_0}{3} \right) v_j^3 \quad (34)$$

The justification for this assumption will be presented later. The substitution of relations (33) and (34) into (9) yields

$$\frac{\partial b}{\partial N_i} = \left(\frac{4\alpha_0^3 \pi \gamma_0}{3} \right) \frac{N_i}{2g_i N} e^{-W_i/kT + \theta_i} \sum_{j=1}^{\infty} g_j (v_j + v_i)^3 e^{W_j/kT - \theta_j}$$

But it is known from statistical mechanics* that the internal partition function may be defined as

$$Q_{int} = \frac{g_i N}{N_i} \quad (35)$$

and from the Fermi equation

$$Q_{int} = e^{-W_i/kT} \sum_{j=1}^{\infty} g_j e^{W_j/kT - \theta_j} = e^{-W_i/kT} \sum_{j=1}^{\infty} g_j$$

* Cf. Ref. 12, p. 116.

The equation for $\frac{\partial b}{\partial N_i}$ may be written

$$\theta_i \equiv \frac{P}{kT} \left(\frac{\partial b}{\partial N_i} \right) = \frac{\beta e^{\theta_i} \sum_{j=1}^{\infty} (v_j + v_i)^3 g_j e^{W_j/kT - \theta_j}}{\sum_{j=1}^{\infty} q_j} \quad (36)$$

where the state parameter β is defined by

$$\beta \equiv \left(\frac{4\pi a_0^3 \gamma_0}{3} \right) \frac{P}{2kT} \quad (37)$$

Equation (36) may be expanded

$$\theta_i \equiv \beta e^{\theta_i} \left\{ v_i^3 + 3v_i^2 \frac{\sum_{j=1}^{\infty} v_j q_j}{\sum_{j=1}^{\infty} q_j} + 3v_i \frac{\sum_{j=1}^{\infty} v_j^2 q_j}{\sum_{j=1}^{\infty} q_j} + \frac{\sum_{j=1}^{\infty} v_j^3 q_j}{\sum_{j=1}^{\infty} q_j} \right\}$$

This relation can be simplified by means of the following definitions:

$$\mu \equiv \frac{3 \sum_{j=1}^{\infty} v_j q_j}{\sum_{j=1}^{\infty} q_j} \quad \delta \equiv \frac{3 \sum_{j=1}^{\infty} v_j^2 q_j}{\sum_{j=1}^{\infty} q_j} \quad \tau \equiv \frac{\sum_{j=1}^{\infty} v_j^3 q_j}{\sum_{j=1}^{\infty} q_j} \quad (38)$$

Thus

$$\theta_i = \beta e^{\theta_i} (v_i^3 + \mu v_i^2 + \delta v_i + \tau) \quad (39)$$

And note that

$$\theta_i = \beta e^{\theta_i} (v_i^3 + \mu v_i^2 + \delta v_i + \tau) \quad (40)$$

As a convenience in terminology we shall refer to μ , δ and τ as the first, second and third "moments" respectively of the internal partition function.

The internal partition function given by the Fermi equation may be written in terms of the moments μ , δ and τ .

$$Q_{int} = e^{-W_i/kT} \sum_{j=1}^{\infty} g_j e^{W_j/kT - \beta e^{\theta_1} (v_j^3 + \mu v_j^2 + \delta v_j + \tau)} \quad (41)$$

Or, in the notation of Equation (26),

$$Q_{int} = e^{-W_i/kT} \left\{ \sum_{j=1}^{\lambda} q_j + 2g_c \sum_{n=a}^{\infty} e^{\alpha/n^2} \sum_{l=0}^{n-1} (2l+1) e^{-\beta e^{\theta_1} (v_n^3 + \mu v_n^2 + \delta v_n + \tau)} \right\}$$

It is assumed here that v_n is a function only of n , and it will be shown later that in fact $v_n = n^2$ in the range wherein the hydrogen-like approximation is valid. The moments μ , δ and τ are independent of l . Thus the above expression reduces to

$$Q_{int} = e^{-W_i/kT} \left\{ \sum_{j=1}^{\lambda} q_j + 2g_c \sum_{n=a}^{\infty} n^2 e^{\alpha/n^2 - \beta e^{\theta_1} (n^6 + \mu n^4 + \delta n^2 + \tau)} \right\} \quad (42)$$

where the well-known relation $\sum_{l=0}^{n-1} (2l+1) = n^2$ has been applied.

The unknowns μ , δ and τ defined by Equations (38) determine the weighting function $e^{-\theta_l}$ by means of relation (39). This equation exhibits the direct dependence of θ_j on the atomic volume b_j through the term $\beta e^{\theta_1} v_j^3$ (Cf. Equation (34)). This term is

essentially the solution obtained by both Fermi and Urey in their investigations. It is important to note that all four terms in θ_j must be included in the evaluation of the weighting function. In fact, for those terms Q_j which make the largest contribution to Q_{int} , the effect of each of the factors involving the three moments are equally important and of the same order of magnitude as the atomic volume term, $\beta e^{\theta_1} v_j^3$. For the larger values of β ($T < 3000^\circ K, P > 1 \text{ atm.}$), the major contribution to the internal partition function is from the lower energy states, as is well known. The relatively small magnitude of $e^{-\theta_j}$ causes the rapid convergence of the series (Cf. Equation (22)) so that the higher energy states make in all negligibly small contributions to Q_{int} . The function θ_j behaves essentially like j^6 , and its value for the lower energy states is small relative to W_j/kT . (Cf. Equation (39)). Because of this fact its exact value is inconsequential, and the inclusion of only the volume term $\beta e^{\theta_1} v_j^3$ yields a suitable order of magnitude estimate. Thus the approximation suggested by Urey of using only this term in θ_j serves to demonstrate the convergence of the partition function, and is not meant to yield an accurate computation of the function. For the larger values of β good estimates of Q_{int} can be obtained readily from the first few terms of the infinite series. This is not the case for smaller values of β (T large, P small). Here the major contribution to Q_{int} stems from the higher energy states wherein θ_j is of the order of the energy term W_j/kT . An accurate estimate of θ_j is therefore required, and one cannot omit the terms involving the moments μ , δ and τ . Obviously the Urey approximation is no longer valid, and a more exact solution must be sought.

It is evident from Equations (38) that the evaluation of the weighting function requires the solution of three simultaneous transcendental equations for the quantities μ , δ and τ . It is noted that each of these relations involves the factor βe^{θ_1} through the terms q_j . If we define this factor $\tilde{\beta} = \beta e^{\theta_1}$, then

$$\tilde{\beta} = \beta e^{\beta(v_1^3 + \mu v_1^2 + \delta v_1 + \tau)}$$

But $\tilde{\beta}(v_1^3 + \mu v_1^2 + \delta v_1 + \tau) \ll 1$; therefore,

$$\tilde{\beta} \approx \frac{\beta}{1 - \beta(v_1^3 + \mu v_1^2 + \delta v_1 + \tau)}$$

When $\beta < 10^{-6}$ the τ term in the bracket above is predominant, and the entire factor is well approximated by $\beta\tau$. Thus

$$\tilde{\beta} \approx \frac{\beta}{1 - \beta\tau} \quad (43)$$

At lower temperatures ($\beta > 10^{-6}$), the terms μv_1^2 and δv_1 may be $O(\tau)$ so that they can no longer be neglected; however, in these cases the entire bracketed term is so small that it may be entirely neglected as compared to 1. Thus the expression (43) is applicable to the larger values of β as well as to the relatively small values for which it was specifically derived.

The substitution of the approximation (43) into Equations (40) and (27) yields

$$q_j \approx g_j e^{W_j/kT - \frac{\beta}{1-\beta\tau}(v_j^3 + \mu v_j^2 + \delta v_j + \tau)}$$

It is convenient to introduce a quantity q such that

$$Q_{int} \equiv q e^{-W_i/kT} \quad (44)$$

Then

$$q = \sum_{j=1}^{\infty} q_j = \sum_{j=1}^{\infty} g_j e^{w_j/kT - \frac{\beta}{1-\beta\tau}(\nu_j^3 + \mu\nu_j^2 + \delta\nu_j + \tau)} \quad (45)$$

Obviously

$$\begin{aligned} \sum_{j=1}^{\infty} \nu_j q_j &= -\left(\frac{1-\beta\tau}{\beta}\right) \frac{\partial q}{\partial \delta} \\ \sum_{j=1}^{\infty} \nu_j^2 q_j &= -\left(\frac{1-\beta\tau}{\beta}\right) \frac{\partial q}{\partial \mu} \\ \sum_{j=1}^{\infty} \nu_j^3 q_j &= \left(\frac{1-\beta\tau}{\beta}\right)^2 \frac{\partial^2 q}{\partial \mu \partial \delta} \end{aligned} \quad (46)$$

so that

$$\begin{aligned} \mu &= -\frac{3(1-\beta\tau)}{\beta q} \frac{\partial q}{\partial \delta} \\ \delta &= -\frac{3(1-\beta\tau)}{\beta q} \frac{\partial q}{\partial \mu} \\ \tau &= \frac{1}{q} \left(\frac{1-\beta\tau}{\beta}\right)^2 \frac{\partial^2 q}{\partial \mu \partial \delta} \end{aligned} \quad (47)$$

It is more convenient to define

$$\begin{aligned} \Phi(\mu, \delta, \tau) &\equiv q\mu + \frac{3}{\beta}(1-\beta\tau) \frac{\partial q}{\partial \delta} = 0 \\ \chi(\mu, \delta, \tau) &\equiv q\delta + \frac{3}{\beta}(1-\beta\tau) \frac{\partial q}{\partial \mu} = 0 \\ \psi(\mu, \delta, \tau) &\equiv q\tau - \left(\frac{1-\beta\tau}{\beta}\right)^2 \frac{\partial^2 q}{\partial \mu \partial \delta} = 0 \end{aligned} \quad (48)$$

A practical method for solving these simultaneous equations for the unknowns μ , δ and τ consists of a simple iteration procedure based on initial estimates for these quantities. If these values are denoted by μ_0 , δ_0 and τ_0 , then the functions Φ , χ and ψ may be expanded

in a Taylor series about the point $(\mu_0, \delta_0, \tau_0)$. Thus, for example

$$\phi(\mu, \delta, \tau) = \phi(\mu_0, \delta_0, \tau_0) + \left(\frac{\partial \phi}{\partial \mu}\right)_0 \Delta\mu + \left(\frac{\partial \phi}{\partial \delta}\right)_0 \Delta\delta + \left(\frac{\partial \phi}{\partial \tau}\right)_0 \Delta\tau + \dots \quad (49)$$

with similar expressions for the other two functions. If only the linear terms are retained, then the three expansions reduce to three linear simultaneous equations in the deviations $\Delta\mu$, $\Delta\delta$ and $\Delta\tau$. The application of these first order corrections to the initial estimates μ_0 , δ_0 and τ_0 yield a second, more accurate solution. The process can be repeated until the desired degree of accuracy is obtained.

B. Internal Partition Function

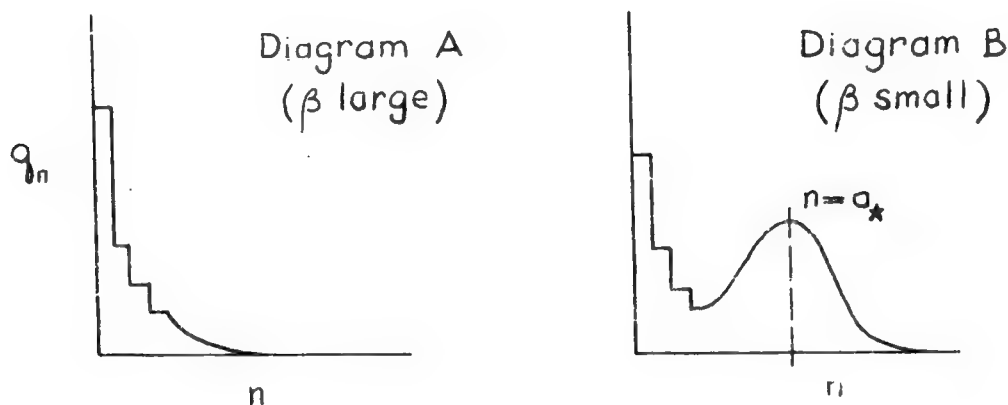
Evidently a closed form expression for q would be useful for the purpose of solving Equations (47). Such an expression for q may be obtained by deriving a suitable approximation for the function

q_n , where

$$q_n \equiv 2g_n^2 e^{\alpha/n^2 - \frac{\beta}{1-\beta\tau}(n^6 + \mu n^4 + \delta n^2 + \tau)}$$

according to the notation of Equation (42). Clearly, this function represents the individual terms of Q_{int} for the higher energy states. If one plots the contributions to Q_{int} from each value of n (i.e. the terms q_n) as a function of n , the area under the function will represent Q_{int} . It should be noted that the lower terms in the finite sum of Equation (42) must be collected for given n . Now it can be shown that for relatively large values of the state parameter β , the function q_n has the form indicated by Diagram A, whereas for

relatively small values of β , q_n behaves essentially as shown in Diagram B.



The step-like nature of q_n for small n represents the terms of the finite sum in Equation (42). The evaluation of the partition function for the cases represented by Diagram A is a relatively minor problem. Indeed, it is of the type which one encounters at the lower temperatures. For these cases the first few terms q_1, q_2, \dots, q_r yield a sufficiently accurate estimate of Q_{int} , and one can neglect the corrections due to the moments μ , δ , and τ . For the more highly excited systems, however, the influence of μ , δ and τ on Q_{int} is appreciable; consequently, these terms must be included.

The partition function Q_{int} is proportional to q (Cf. Equation (44)); therefore, it is of interest to consider the evaluation of the infinite series (45). The Euler-Maclaurin formula⁽¹⁸⁾ may be applied for this purpose. If (45) is written in the form of Equation (42), and the infinite series in the expression approximated by the first two terms of the formula, then

$$q \approx \sum_{j=1}^{\infty} q_j + \int_a^{\infty} q(n) dn + \frac{1}{2} q(a) \quad (50)$$

The function $q(n)$ is

$$q(n) \equiv 2g_c n^2 e^{\alpha/n^2 - \tilde{\beta}(n^6 + \mu n^4 + \delta n^2 + \tau)} \equiv 2g_c n^2 h(n) \quad (51)$$

The problem is to evaluate the integral of Equation (50). Unfortunately the integral of $q(n)$ even in its present form is an unusually complicated function and is not amenable to any elementary methods of analysis. Numerical calculations indicate, however, that the function $h(n)$ defined by Equation (51) may be approximated in the neighborhood of some value $n=a_*$ by a linear function (Cf. Figure 2). Therefore, we expand $h(n)$ in a Taylor series about the point $n=a_*$ and take the first two terms.

$$h(y) = h(a_*) + h'(a_*)(y - a_*) + \dots \quad (52)$$

where

$$h(a_*) \equiv e^{\alpha/a_*^2 - \tilde{\beta}(a_*^6 + \mu a_*^4 + \delta a_*^2 + \tau)}$$

$$h'(a_*) \equiv -2 \left[\frac{\alpha}{a_*^3} + \tilde{\beta}(3a_*^5 + 2\mu a_*^3 + \delta a_*) \right] h(a_*)$$

If these expressions are substituted into the above mentioned integral, then

$$\int_a^\infty q(y) dy \simeq 2g_c \int_a^{a_\infty} y^2 [h(a_*) + h'(a_*)(y - a_*)] dy$$

The upper limit ∞ has been replaced by a_∞ which denotes the zero of the approximation (52). The integral is terminated at a_∞ in order to avoid the negative values predicted by the approximation.

$$a_{\infty} = a_{\star} - \frac{h(a_{\star})}{h'(a_{\star})} \quad (53)$$

The substitution of this relation into the integral yields

$$\int_a^{\infty} q(y) dy \approx 2 g_c h'(a_{\star}) a_{\infty}^4 \left\{ -\frac{1}{3} \left[1 - \left(\frac{a}{a_{\infty}} \right)^4 \right] + \frac{1}{4} \left[1 - \left(\frac{a}{a_{\infty}} \right)^3 \right] \right\}$$

This expression can be simplified by a suitable choice of a_{\star} which denotes some convenient point in the range of $h(y)$ wherein the approximation (52) is valid. In this region the function θ_j , which may be represented by $\tilde{\beta} n^6$, is of order one. Thus we are interested in values of $n = O(\tilde{\beta}^{-\frac{1}{6}})$. Let us select, therefore, the following value for a_{\star} :

$$a_{\star} \equiv (13\beta)^{-\frac{1}{6}} \quad (54)$$

This assumption will be applied to all calculations so long as β is sufficiently small to yield values of $a_{\star} > a$. If the value computed from Equation (54) is less than a , then the value a will be assumed instead.

The particular merit of assumption (54) lies with the fact that for small β , the function $q(n)$ behaves as indicated in Diagram B, and $(13\beta)^{-\frac{1}{6}}$ is a good approximation to the maximum point of this function. If Equation (54) yields a value for $a_{\star} > a$, then a_{\star} is indeed a maximum point of the function $q(n)$, and it follows by differentiation of Equation (51) that

$$h(a_{\star}) = -\frac{a_{\star}}{2} h'(a_{\star})$$

The substitution of this relation into Equation (53) yields

$$a_{\infty} = \frac{3}{2} a_*$$

and

$$\int_a^{\infty} q(y) dy \approx \epsilon a_*^3 h(a_*)$$

where

$$\epsilon = \epsilon(a, a_*) = g_c \frac{27}{16} \left\{ 4 \left[1 - \left(\frac{a}{a_{\infty}} \right)^3 \right] - 3 \left[1 - \left(\frac{a}{a_{\infty}} \right)^4 \right] \right\}$$

The internal partition function may be approximated by means of the above relations. Thus

$$q = Q_{int} e^{W_i/kT} = \sum_{j=1}^{\lambda} q_j + \frac{1}{2} q(a) + \epsilon a_*^3 h(a_*) \quad (55)$$

The second and third terms represent the infinite series as previously indicated.

Figure 3 exhibits the accuracy with which the function $q(n)$ can be approximated for both small and large values of β according to the relations developed above. For small β , the approximation provides an adequate match to the true function in the neighborhood of the maximum contribution of $q(n)$ to Q_{int} . For larger β , the comparison is not as good. In fact, because of the selection of a_* according to Equation (54) and the assumption of zero slope for $q(n)$ at a_* , the approximate function has neither the correct slope or curvature. This problem was investigated in more detail in order to obtain a better match. An improvement upon the above mentioned method was attempted by inserting the correct value of the slope for $q(n)$ at $n=a_*$ and by considering various other positions for a_* . In none of the

cases investigated, however, did the corrected relations yield as good an estimate of the integral (Cf. Equation (50)), as the proposed approximations. It appears that this method is the best if only the linear term is to be retained in the expansion of $h(y)$. The accuracy can be improved however if the curvature term is included. For the present analysis the two term expansion will be sufficiently accurate.

The actual function $q(n)$ is compared graphically in Figure 3 with the approximate expression involving the two-term expansion of $h(n)$ as indicated in Equation (52). The actual sum is also compared with the two-term Euler-Maclaurin expansion, and for both values of temperature, the agreement was found to be good. Computations indicate that for $T=5000$ the error in Q_{int} is less than 1 percent, whereas for $T=20000$, the error is less than 9 percent

The approximation to q given by Equation (55) may be applied to the solution of the simultaneous Equations (47). The corresponding relations are

$$\begin{aligned}\mu &= \frac{3}{q} \left\{ q^{(1)} + \frac{a^2}{2} q(a) + \epsilon a_*^5 h(a_*) \right\} \\ \delta &= \frac{3}{q} \left\{ q^{(2)} + \frac{a^4}{2} q(a) + \epsilon a_*^7 h(a_*) \right\} \\ \tau &= \frac{1}{q} \left\{ q^{(3)} + \frac{a^6}{2} q(a) + \epsilon a_*^9 h(a_*) \right\}\end{aligned}\tag{56}$$

where the notation

$$q^{(4)} \equiv \sum_{j=1}^{\lambda} \nu_j^4 q_j\tag{57}$$

has been introduced. The solution of Equations (56) by the suggested iteration procedure is straightforward but lengthy. For this reason the derivatives indicated in Equation (49) have been computed and summarized in Appendix C.

It is a relatively minor problem, however, to investigate the solution of these equations for the extreme values of temperature. At very large temperatures the major contribution to the internal partition function is from the higher energy states. Therefore, the $\epsilon a_*^3 h(a_*)$ term in Equation (55) is predominant, and a good approximation to q is,

$$\lim_{T \rightarrow \infty} q = \epsilon a_*^3 h(a_*)$$

Therefore, by neglecting the first two terms in each of the Equations (56), we obtain immediately the following asymptotic values for the three moments:

$$\mu = 3a_*^2 \quad \delta = 3a_*^4 \quad \gamma = a_*^6 \quad (58)$$

We are concerned here with the case for $\beta \rightarrow 0$. Thus the function $q(n)$ is of the type indicated in Diagram B, and a_* represents in fact the maximum point of the function. It is possible to derive the appropriate value of a_* from the asymptotic expressions developed above. The condition of zero slope for $q(n)$ at $n=a_*$, along with the values given in Equations (58), yield the following equation in a_* :

$$13\beta a_*^8 - \alpha \beta a_*^6 - a_*^2 + \alpha = 0 \quad (59)$$

For the cases in question a representative set of the relative magnitudes involved are $\alpha, a_* = O(10)$ and $\beta = O(10^{-6})$. Therefore, one can

obtain an approximate solution to Equation (59) by neglecting the α_{\star}^6 and α terms. The corresponding solution is the relation previously assumed for α_{\star} and presented as Equation (54).

The investigation of the solutions for the simultaneous Equations (47) in the limit for very low temperatures also yields a set of simple expressions for the moments. For this case the major contribution to Q_{int} is from the first term (ground state). Therefore, if we neglect all others, then

$$q \simeq q_1$$

and

$$q^{(1)} \rightarrow \nu_1 q_1 \quad q^{(2)} \rightarrow \nu_1^2 q_1 \quad q^{(3)} \rightarrow \nu_1^3 q_1$$

If these expressions are substituted into Equations (47), one obtains readily the low temperature solutions for the three moments.

$$\mu = 3\nu_1 \quad \delta = 3\nu_1^2 \quad \tau = \nu_1^3 \quad (60)$$

These two sets of solutions, Equations (58) and (60) can be used effectively as the initial estimates μ_0 , δ_0 and τ_0 which are required in the iteration procedure outlined above. Figure 4 gives the exact solution to the simultaneous Equations (56) as a function of temperature for a given pressure. It is interesting to compare these solutions with the high temperature approximations (broken line curves) which have also been included and to note the asymptotic behavior of the two sets of curves.

V. ATOMIC VOLUMES

A. Hydrogen-like Model

In the present section we examine a method for computing the atomic volumes b_j which determines the weighting function according to Equation (12). For the purpose of computing thermodynamic functions, it will be desirable to sacrifice accuracy for the sake of simplicity and to consider approximate methods. In order to obtain some information regarding probable errors incurred by the approximations, the familiar method of screening constants^(4, 5) was applied as the approximate technique, and the results in a few particular cases compared with more accurate solutions obtained by the Hartree method.⁽⁶⁾ The present discussion is confined to a review of the approximate method.

The application of the method of screening constants to the calculation of atomic volumes consists of treating a given atom as an hydrogen-like atomic structure. This approximation would appear to be reasonable, especially for the higher electronic states, on the basis of the argument already given in Section III B. For the lower energy states, the shielding effect of the outer electrons is not as effective; hence, it is necessary to apply corrections in the computation of the effective core charge by means of empirical rules. Slater suggests a set of rules⁽⁴⁾ based on data obtained from ions, x-ray energy levels, etc. The total shielding effect of the outer electrons on the field of the nucleus is determined by computing the contributions of each electron by means of the rules.

The method is readily applied to volume calculations, and is therefore especially suited to the present problem.

It was previously noted that the term values for the hydrogen atom can be approximated by the Bohr model.

$$W_{nl} \simeq \frac{Z^2 R_0 hc}{n^2} \quad (25)$$

where Z , (the atomic number) is of course one. If the many-electron atom is treated as an hydrogen-like structure, it is necessary to introduce an effective atomic number Z_{eff} which is defined

$$Z_{\text{eff}} \equiv (Z - S) \quad (61)$$

where S is the screening constant computed by the method indicated above. The analogous energy relation (in Rydberg units) to expression (25) is, therefore

$$\frac{W_{nl}}{R_0 hc} = \epsilon_{nl} = \frac{(Z - S)_{nl}^2}{n_{\star}^2} \quad (62)$$

It is assumed that this relation will be valid for any arbitrary atom. Note that spectroscopic data yields ϵ_{nl} which, along with the computed values of S , define n_{\star} .

The calculation of atomic volumes is made on the basis of an assumed spherically symmetric configuration. Thus the determination of the average value of the atomic radius cubed ($\overline{r^3}$) is required. This quantity may be computed readily from the relation

$$\overline{r^3} = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \Psi^* r^3 \Psi r^2 dr \sin \vartheta d\vartheta d\varphi$$

where r , ϑ and φ denote the polar coordinates, and Ψ is the wave function of the system in question.

In the case of the hydrogen atom it is known that the wave function is given by ⁽¹⁹⁾

$$\Psi = \bar{\Psi}(r, \vartheta, \varphi) = R_{nl}(r) S_{lm}(\vartheta, \varphi) \quad (63)$$

$S_{lm}(\vartheta, \varphi)$ is a normalized surface harmonic of order $|m|$ and degree l , and $R_{nl}(r)$ is defined as

$$R_{nl}(r) \equiv - \left\{ \left(\frac{2Z}{na_0} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{\frac{1}{2}} e^{-\eta/2} \eta^l L_{n+l}^{2l+1}(\eta)$$

$L_{n+l}^{2l+1}(\eta)$ is the associated Laguerre polynomial of degree $(l-n)$ and order $2l+1$, and $\eta = 2Zr/na_0$ with a_0 = radius of the first Bohr orbit. It follows, therefore, that

$$\overline{\left(\frac{r}{a_0} \right)_{ln}^3} = \left(\frac{n}{2Z} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3} \int_0^\infty e^{-\eta} \eta^{5+2l} L_{n+l}^{2l+1}(\eta)^2 d\eta \quad (64)$$

The integral may be readily evaluated to yield (Cf. Appendix B)

$$\left[(n+l)! 4! \right]^2 \sum_{t=0}^4 \frac{(n+l+4-t)!}{[(4-t)! t!]^2 (n-l-1-t)!} \quad (B-14)$$

It should be noted that this sum terminates at $t=n-l-1$ if $n-l < 5$.

If the summation is expanded out and the resulting expression substituted into Equation (64), then

$$\begin{aligned} \overline{\left(\frac{r}{a_0} \right)_{ln}^3} = & \frac{1}{16} \left(\frac{n^2}{Z} \right)^3 \left(1 + \frac{l+4}{n} \right) \cdots \left(1 + \frac{l+1}{n} \right) \left\{ 1 + \frac{16(n-l-1)}{n+l+4} \right. \\ & \left. + \frac{36(n-l-1)(n-l-2)}{(n+l+4)(n+l+3)} + \frac{16(n-l-1) \cdots (n-l-3)}{(n+l+4) \cdots (n+l+2)} + \frac{(n-l-1) \cdots (n-l-4)}{(n+l+4) \cdots (n+l+1)} \right\} \end{aligned}$$

which may be reduced to

$$\overline{\left(\frac{r}{a_0}\right)^3}_{\ell n} = \left(\frac{n^2}{Z}\right)^3 \left\{ 3\left(\frac{\ell}{n}\right)^4 + \frac{6(\ell)}{n}\left(\frac{\ell}{n}\right)^3 - 3\left(\frac{\ell}{n}\right)^2\left(10 + \frac{1}{n^2}\right) - \frac{6(\ell)}{n}\left(5 + \frac{1}{n^2}\right) + \left(35 + \frac{25}{n^2}\right) \right\} \quad (65)$$

Or, if the quantity in the brackets is denoted by $\gamma_{\ell n}$, then

$$\overline{\left(\frac{r}{a_0}\right)^3}_{\ell n} = \left(\frac{n^2}{Z}\right)^3 \gamma_{\ell n} \quad (66)$$

An analogous relation may be assumed for the many-electron atom by replacing the (n^2/Z) factor by Equation (62).

$$\overline{\left(\frac{r}{a_0}\right)^3}_{\ell n} = \left(\frac{Z-S}{\varepsilon}\right)^3 \gamma_{\ell n} \equiv \nu_{\ell n}^3 \gamma_{\ell n} \quad (67)$$

The spherical volume b_i corresponding to this value of $(r^3)_i$ is

$$b_i = \left(\frac{4\pi a_0^3}{3}\right) \gamma_i \nu_i^3 \quad (68)$$

where the more general notation i for the quantum energy state has been introduced. It is evident from Equation (26) that in computing the internal partition function, it is necessary to sum the product of the degeneracy and the weighting function $g_{\ell n} e^{-\theta_{\ell n}}$ over the allowed values of ℓ . The computation is complicated by the presence of the function $\gamma_{\ell n}$, which is defined by Equation (66). Figure 5 gives some indication of the nature of this function. Note that $1 \leq \gamma_{\ell n} \leq \frac{35}{8}$ and also that

$$\gamma_{0,n} = \frac{1}{8} \left(35 + \frac{25}{n^2} \right)$$

$$\gamma_{n-1,n} = 1 + \frac{3}{n} + \frac{11}{4n^2} + \frac{3}{4n^3}$$

A general approximation can be obtained from Equation (65) for small l/n .

$$Y_{ln} \simeq \frac{35}{8} \left[1 - \frac{6}{7} \left(\frac{l}{n} \right)^2 \right]$$

In spite of these simplifications the summation over l proved to be a formidable problem and no simple solution was found. In view of this fact, it seemed advisable to simplify the entire problem by assigning to Y_{ln} some average value Y_0 . Equation (34) is the corresponding simplification of the general expression (68).

The selection of Y_0 for a given system can be accomplished by an iteration process. Starting with an initial estimate, one can compute q by first solving for the moments μ , δ and τ . An average value of Y_{ln} can then be defined for each value of n . If the computed average compares favorably with the assumed value in the region of n wherein $q(n)$ makes the largest contribution to q , then the initial estimate was an adequate one. If not, then the process can be repeated. A suitable average Y_{ln} for given n can be defined as

$$e^{-\tilde{B}(n^6 Y_0 + \mu n^4 Y_0^{\frac{2}{3}} + \delta n^2 Y_0^{\frac{1}{3}})} \equiv \frac{1}{n^2} \sum_{l=0}^{n-1} (2l+1) e^{-\tilde{B}(n^6 Y_{ln} + \mu n^4 Y_{ln}^{\frac{2}{3}} + \delta n^2 Y_{ln}^{\frac{1}{3}})}$$

where

$$\tilde{B} \equiv \frac{\beta}{Y_0}$$

A sample computation $\tilde{B} = 2.3 \times 10^{-8}$

this function as the assumed value is varied from $\gamma_0 = 2$ to $\gamma_0 = 2.6$. The influence of γ_0 on q is also a relatively small effect. Sample calculations indicate that for $\beta = 0(10^{-7})$, a 25% increase in γ_0 causes about a 5% decrease in q .

B. Calculation of Atomic Volumes

Atomic volumes for any quantum energy state i may be computed for a spherical model (based on the assumption of a hydrogen-like structure) by using Equation (67). The quantity ν_i is computed from the known spectroscopic data of the atom (assumed hydrogen-like for the higher states), and the screening constant S , by the method previously mentioned. It is of interest to determine the value of $\nu_i \rightarrow \nu_{ln}$ for the higher energy states according to the hydrogen-like approximations. In these cases, $(Z-S) \rightarrow 1$ and $\epsilon_{ln} = \frac{1}{n^2}$ from Equation (62). It is evident from Equation (67) that

$$\nu_{ln} = \nu_n = n^2$$

and

$$b_i \rightarrow b_{ln} = \left(\frac{4\pi a_0^3}{3} \right) \gamma_{ln} n^6 \quad (69)$$

The calculation of these volumes may also be carried out by applying the more accurate method of Hartree, usually referred to as the method of self-consistent fields. The procedure is essentially a numerical one and relies primarily on the representation of a complex atomic structure by the superposition of single-electron wave functions. A numerical representation of the wave function for the entire system is obtained by trial and error estimates on these single-electron functions. The applicability of the method to the

present problem was investigated by actually carrying out volume computations $\overline{r^3}$ for the potassium atom. The semi-empirical wave functions for this atom were supplied by D. S. Villars of the U. S. Naval Ordnance Test Station, Inyokern. These data were tabulated for the radial wave function $P_{ln}(r)$ as a function of the radial distance from the center of the nucleus. The function $P_{ln}(r)$ is defined

$$P_{ln}(r) = r \dot{R}_{ln}(r)$$

in accordance with the expression for Ψ given by Equation (63). The function $\overline{r^3}$ was readily obtained by the evaluation of the following integral (Cf. previous definition of $\overline{r^3}$) using numerical methods of integration:

$$\overline{r^3} = \int_0^{\infty} P_{ln}^2(r) r^3 dr$$

Sample computations of $\overline{r^3}$ for various energy states are presented in Table I and compared with the results obtained by the method of screening constants. The correlation is well within the limits of acceptable engineering accuracy.

VI. THERMODYNAMIC FUNCTIONS

A. Fundamental Relations

The following well-known relations* define the contribution to the thermodynamic functions by the internal energy states. In the present case Q_{int} is due to electronic excitation.

$$\frac{F}{kT} = -\ln Q_{int} \quad \frac{E}{kT} = \frac{H}{kT} = \frac{1}{Q_{int}} \left(T \frac{\partial Q_{int}}{\partial T} \right) \quad (70)$$

where F is the Gibbs free energy

$$F = H - TS \quad (71)$$

The heat capacity C is

$$\frac{C}{k} = \frac{1}{Q_{int}} \left\{ 2 \left(T \frac{\partial Q_{int}}{\partial T} \right) - \frac{1}{Q_{int}} \left(T \frac{\partial Q_{int}}{\partial T} \right)^2 + \left(T^2 \frac{\partial^2 Q_{int}}{\partial T^2} \right) \right\} \quad (72)$$

The evaluation of these functions requires explicit relations for Q_{int} and its first two temperature derivatives. These derivatives may be computed in general form directly from the Fermi Equation.

B. Thermodynamic Functions

Good approximations for the thermodynamic functions can be obtained by using Equation (55) for Q_{int} and performing the necessary differentiations directly on this expression. In carrying out this scheme, it is convenient to separate Q_{int} into two parts corresponding to the notation of Equation (26). Thus define

* Cf. Reference 10, p. 442.

$$Q_{int} \equiv Q^{(0)} + Q^{(1)}$$

where according to Equation (55)

$$Q^{(0)} \equiv e^{-W_1/kT} \sum_{j=1}^{\lambda} q_j$$

$$Q^{(1)} \equiv Q_o^{(1)} + Q_{\star}^{(1)} \equiv \frac{1}{2} q(a) e^{-W_1/kT} + \epsilon a_{\star}^3 h(a_{\star}) e^{-W_1/kT}$$

The first derivative of Q_{int} with respect to T is

$$T \frac{\partial Q_{int}}{\partial T} = T \frac{\partial Q^{(0)}}{\partial T} + T \frac{\partial Q_o^{(1)}}{\partial T} + T \frac{\partial Q_{\star}^{(1)}}{\partial T} \quad (73)$$

where

$$T \frac{\partial Q^{(0)}}{\partial T} = e^{-W_1/kT} \left\{ \sum_{j=1}^{\lambda} \left(\frac{w_j}{kT} \right) q_j + \frac{\beta}{(1-\beta\tau)^2} [q^{(3)} + \mu q^{(2)} + \delta q^{(1)} + \tau q^{(0)}] \right\}$$

$$T \frac{\partial Q_o^{(1)}}{\partial T} = Q_o^{(1)} A(a)$$

$$T \frac{\partial Q_{\star}^{(1)}}{\partial T} = Q_{\star}^{(1)} A(a_{\star})$$

and

$$A(a) \equiv \frac{w_a}{kT} + \beta \frac{(a^6 + \mu a^4 + \delta a^2 + \tau)}{(1-\beta\tau)^2}$$

$$w_a \equiv W_1 - \frac{R_o h c}{a^2}$$

The second derivative of Q_{int} is

$$T^2 \frac{\partial^2 Q_{int}}{\partial T^2} = T^2 \frac{\partial^2 Q^{(0)}}{\partial T^2} + T^2 \frac{\partial^2 Q_o^{(1)}}{\partial T^2} + T^2 \frac{\partial^2 Q_{\star}^{(1)}}{\partial T^2} \quad (74)$$

where

$$\begin{aligned}
 T^2 \frac{\partial^2 Q^{(0)}}{\partial T^2} &= e^{-W_1/kT} \left\{ -2 \sum_{j=1}^{\lambda} \left(\frac{w_j}{kT} \right) q_j + \sum_{j=1}^{\lambda} \left(\frac{w_j}{kT} \right)^2 q_j - \frac{2\beta}{(1-\beta\tau)^3} [q^{(3)} + \mu q^{(2)} + \delta q^{(1)} + \tau q^{(0)}] \right. \\
 &\quad + \frac{\beta^2}{(1-\beta\tau)^4} [q^{(6)} + 2\mu q^{(5)} + (2\delta + \mu^2) q^{(4)} + 2(\tau + \mu\delta) q^{(3)} + (2\mu\tau + \delta^2) q^{(2)} \\
 &\quad \left. + 2\delta\tau q^{(1)} + \tau^2 q^{(0)}] + \frac{2\beta}{(1-\beta\tau)^2} \sum_{j=1}^{\lambda} \left(\frac{w_j}{kT} \right) (\nu_j^3 + \mu\nu_j^2 + \delta\nu_j + \tau) q_j \right\} \\
 T^2 \frac{\partial^2 Q_0^{(0)}}{\partial T^2} &= Q_0^{(0)} \left\{ A^2(a) - \frac{2W_0}{kT} - \frac{2\beta}{(1-\beta\tau)^2} (a^6 + \mu a^4 + \delta a^2 + \tau) \right\} \\
 T^2 \frac{\partial^2 Q_{\star}^{(0)}}{\partial T^2} &= Q_{\star}^{(0)} \left\{ A^2(a_{\star}) - \frac{2W_{\star}}{kT} - \frac{2\beta}{(1-\beta\tau)^2} (a_{\star}^6 + \mu a_{\star}^4 + \delta a_{\star}^2 + \tau) \right\}
 \end{aligned}$$

The substitution of these derivatives into the expressions for the thermodynamic functions, Equations (70) to (72), is a straightforward procedure.

C. Equation of State

An equation of state for a gaseous system of neutral atoms with excited electronic states can be derived in terms of the results which have already been obtained in the previous sections. In particular, it can be shown that the covolume correction b given in Equation (1) and defined in Equation (4) may be expressed as a function of the moments of the internal partition function (Cf. Equations (38)) and the state parameter β .

Consider, therefore, the general relation (4). This expression may be simplified considerably by introducing the relations

(27), (33) to (35) and (44). Thus

$$\frac{b}{b_0 N} = \frac{1}{q^2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (v_i + v_j)^3 q_j q_i$$

where

$$b_0 \equiv \frac{2\pi a_0^3 \gamma_0}{3} \quad (75)$$

If the above result is expanded

$$\frac{b}{b_0 N} = \frac{1}{q^2} \sum_{i=1}^{\infty} q_i \left\{ v_i^3 \sum_{j=1}^{\infty} q_j + 3v_i^2 \sum_{j=1}^{\infty} v_j q_j + 3v_i \sum_{j=1}^{\infty} v_j^2 q_j + \sum_{j=1}^{\infty} v_j^3 q_j \right\}$$

Obviously

$$\frac{b}{b_0 N} = \frac{1}{q} \sum_{i=1}^{\infty} q_i \left\{ v_i^3 + \mu v_i^2 + \delta v_i + \tau \right\}$$

And so

$$\frac{b}{b_0 N} = 2 \left(\tau + \frac{\delta \mu}{3} \right) \quad (76)$$

The corresponding equation of state is readily obtained by substituting this relation into Equation (1), which, in standard form is

$$\frac{PV}{NkT} = 1 + \frac{bP}{NkT} \simeq 1 + \frac{b}{V} \quad (77)$$

If the definition of β is applied along with Equation (76), the above equation reduces to

$$\frac{PV}{RT} = 1 + 2\beta \left(\tau + \frac{\delta \mu}{3} \right) \quad (78)$$

It is of interest to examine the behavior of this function in the limit for large temperature. According to the analysis of Part IV B above, the high temperature limits to the three moments are given by Equations (58). These results, along with the approximation (54), yield

$$\lim_{T \rightarrow \infty} \left(\frac{PV}{RT} \right) = 1 + \frac{8}{13} \quad (79)$$

Some sample computations of the "compressibility factor" given in (78) are presented in Figures 7, 8 and 9.

The equation of state (78) may be corrected to account for the presence of ions in the gas mixture which appear as products of the reaction (28). In making the actual calculation, it will be more convenient to use a slightly different definition than indicated in Equation (77). Consider therefore the expression

$$\frac{PV}{\eta kT} = 1 + \frac{Pb}{\eta kT} \quad (80)$$

where η denotes the total number of particles at equilibrium according to the definition of Part III-C. The substitution of Equations (29) into (80) yields

$$\frac{PV}{NkT(1+\alpha_1)} = 1 + \frac{Pb}{\eta kT}$$

which is, in the notation of Equation (73)

$$\frac{PV}{NkT} = \left[1 + 2\beta \left(\tau + \frac{\mu\delta}{3} \right) \right] (1+\alpha_1) \quad (81)$$

Note that the limit of the ionization factor for large T is 2.

D. Discussion

The present analysis has achieved three objectives. First, a convergent series expression for the internal partition function of un-ionized atoms has been derived. Second, this result provides a method for computing the electronic contribution to the thermodynamic functions. And finally, the range of applicability of both the customary method and of the covolume treatment has been determined. The results of the analysis show decisively that although the covolume corrections are the major deviations from ideal gas behavior at the lower temperatures, these effects may be neglected in making engineering calculations. Furthermore it is found that at the higher temperatures, when these deviations become significant, it is necessary to include also the effects of ionization. Indeed, actual computations performed for lithium and nitrogen (Cf. Figures 7, 8 and 9) indicate that the non-ideal behavior of the gas at the higher temperatures is due largely to this effect, and that the covolume correction to the equation of state due to the expanding volumes of the excited atoms is in comparison a smaller deviation. Therefore, if these results are at all representative of the general behavior of all atoms, then it is apparent that a realistic derivation of the thermodynamic functions of gases at high temperatures must necessarily take into account the presence of ions and free electrons in the mixture.

The extension of the present treatment to include the effect of ions and free electrons in the mixture is a formidable problem. The most serious complication which arises in this calculation is the specification of the interaction between the various types of particles. Although the method of excluded volumes has been applied to approx -

imate the interaction of neutral atoms in excited electronic states, the application of this method is not generally recommended for systems which contain charged particles. An honest calculation of the thermodynamic functions of a mixture of atoms, ions and electrons must be based on a more realistic description of the interaction potentials; but, these potentials are generally not known.

When ionization is of the order of 10 percent (at temperatures of about $10,000^{\circ}\text{K}$) charged particles will be involved in relatively few encounters, and it is expected that the interaction terms corresponding to binary collisions between charged particles and neutral atoms will yield small corrections on the thermodynamic functions. It is suggested therefore that as a first approximation these interaction effects may be neglected entirely, and that the mixture may be treated by the familiar methods of classical solution thermodynamics. In these calculations one may compute separately the contributions to the thermodynamic functions of the atoms, and of the ions and free electrons and then apply the necessary mixing terms to determine the properties of the complete system. The charged particles in the mixture may be treated by the Debye-Hückel theory⁽²⁰⁾ and the methods outlined in the present study are directly applicable to the neutral atoms. These approximations are admittedly crude, but an attempt to achieve greater accuracy would require much more realistic descriptions of the interactions for the various atomic particles.

The relations derived in the present analysis have been applied to the computation of the thermodynamic functions of lithium I

for various temperatures and pressure. In particular, the contributions from the electronic states to the internal energy, the entropy and the heat capacity have been plotted as functions of temperature in Figures 10 to 12. It should be noted that these functions represent the contributions of only the neutral atoms. Broken-line curves have been drawn for the higher temperature range of the functions because of the uncertainty in the method of computing atomic volumes for the more highly excited atoms. These volumes are relatively small for the lower energy states, and large errors can be tolerated in the calculation. But, the influence of the atomic volumes (i. e. interactions) on the thermodynamic functions become more pronounced at the higher temperatures; thus, more realistic interaction potentials should be introduced for atoms in the highly excited electronic states.

REFERENCES

1. Fermi, E., "Über die Wahrscheinlichkeit der Quantenzustände", Zeits. für Phy. 26, 54 (1924).
2. Urey, H. C., "The Distribution of Electrons in the Various Orbits of the Hydrogen Atom", Astrophysics Journal 59, 1 (1924).
3. Fowler, R. H., "Statistical Mechanics", Cambridge, 2nd Edition Ch. VIII and XIV (1936).
4. Slater, J. C., "Atomic Shielding Constants", Phy. Rev. 36, 57 (1930).
5. Eckart, C., "The Theory and Calculation of Screening Constants", Phy's Rev. 36, 878 (1930).
6. Hartree, D. R., "The Wave Mechanics of an Atom with a Non-Coulomb Central Field", Proc. Cambridge Philosophical Society 24, 89, 111 (1928).
7. Chapman, S. and Cowling, J. C., "Mathematical Theory of Non-Uniform Gases", Cambridge, p. 274 (1939).
8. Guggenheim, E. A., "Thermodynamics", North Holland Publishing Co., Amsterdam, 2nd Edition, p. 59, Chapter VI (1950).
9. Fenner, S. S., JP 201 Class Notes, California Institute of Technology (1950-1951).
10. Mayer, J. E. and Mayer, M. G., "Statistical Mechanics", John Wiley & Sons, Inc. p. 125, (1940).
11. Tolman, R. C., "The Principles of Statistical Mechanics", Oxford University Press, Ch. XIV (1938).
12. Wenner, R. R., "Thermo Chemical Calculations", McGraw-Hill Publishing Co., New York, p. 118 (1941).
13. Rosenfeld, L., "Nuclear Forces", North Holland Publishing Co., Amsterdam, Ch. XIII.
14. Saha, M. N., "Ionization in the Solar Chromosphere", Phil. Mag. 40 472 (1920).
15. Unsöld, A., "Physik der Sternatmosphären", Julius Springer, Berlin, p. 64 (1938).
16. Herzberg, G., "Atomic Spectra and Atomic Structure", Dover Publications, 2nd Edition, p. 126 (1944).

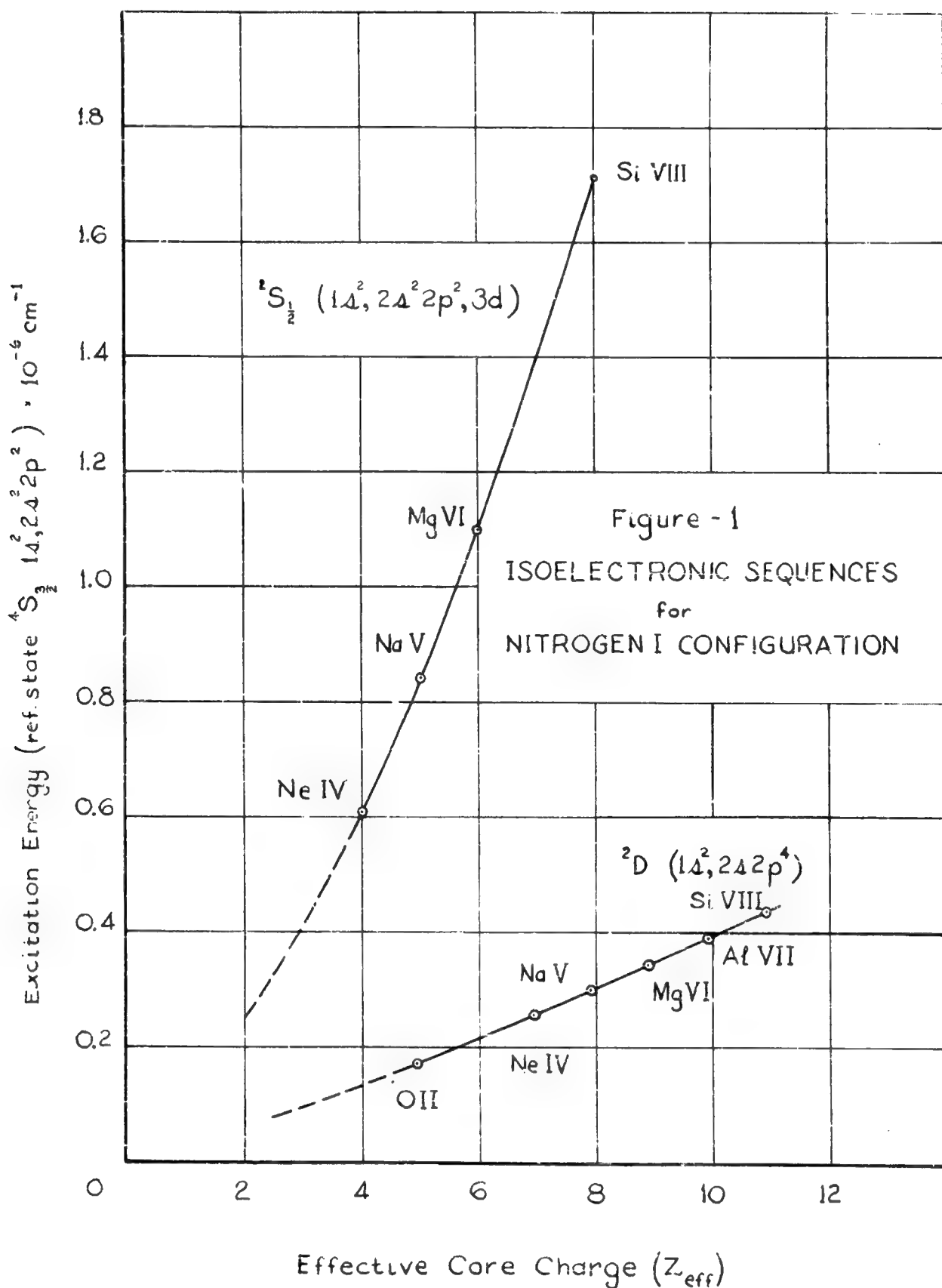
17. White, H. E., "Introduction to Atomic Spectra", McGraw-Hill Publishing Co., New York, Ch. XVII (1934).
18. Whittaker, E. T. and Watson, G. N. "Modern Analysis", Cambridge, 4th Edition, p. 127 (1950).
19. Pauling, L. and Wilson, E. B., "Introduction to Quantum Mechanics", McGraw-Hill Publishing Co., New York, p. 115 (1935).
20. Fowler, R. H. and Guggenheim, E. A., "Statistical Thermodynamics", Cambridge, p. 385 (1949).

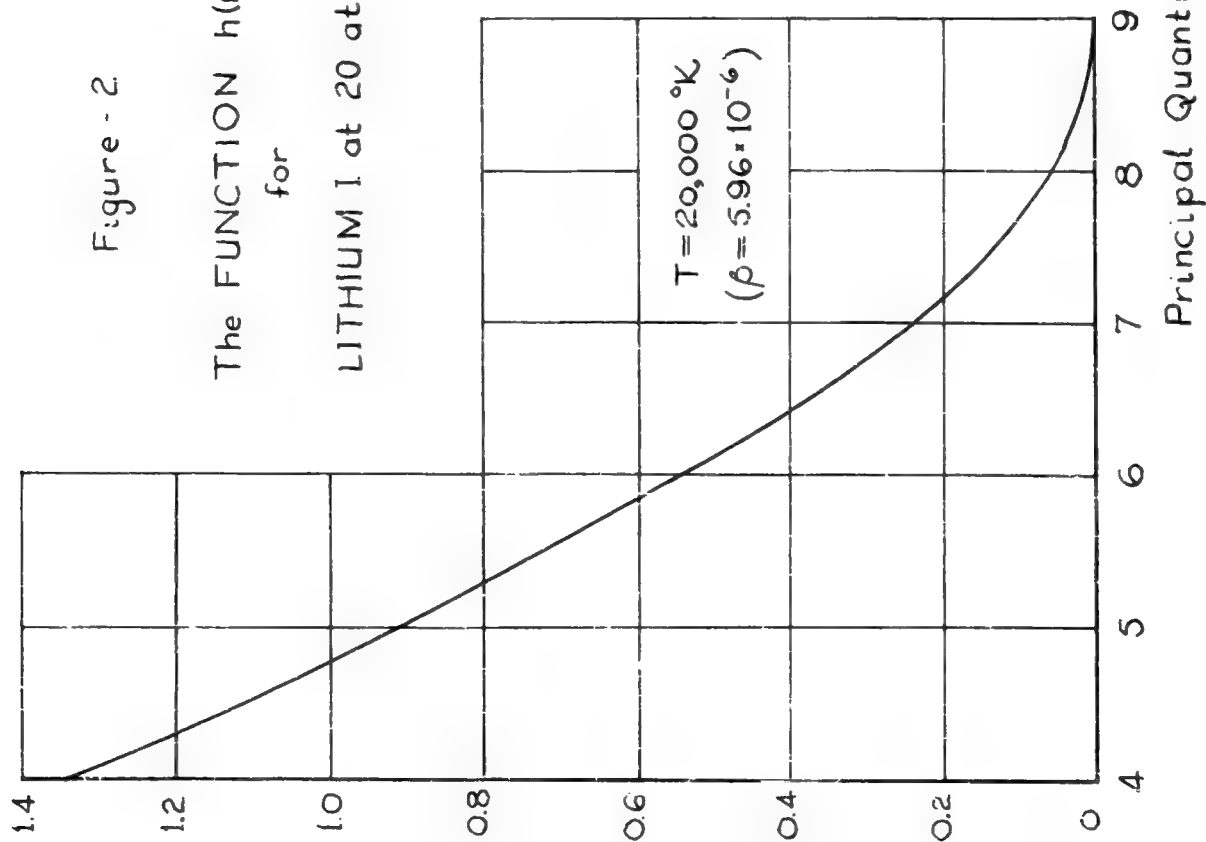
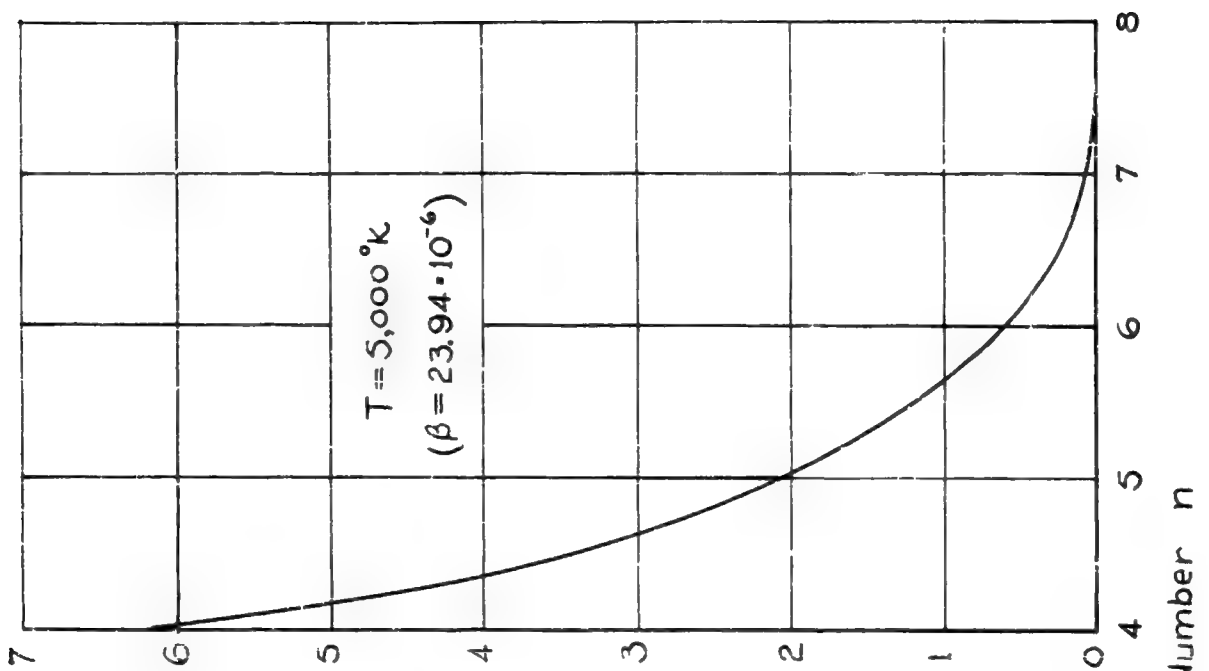
TABLE I. ATOMIC VOLUME CALCULATIONS
FOR POTASSIUM I.

State emission electron	$\left(\frac{Z-S}{\epsilon}\right)_{ln}$	γ_{ln}	$\overline{\left(\frac{r_{ln}}{a_0}\right)^3}$ (Slater's method)	$\overline{\left(\frac{r_{ln}}{a_0}\right)^3}$ (Hartree)
3d	541	2.33	1260	1027
5d	516	4.50	2320	2366
5d	11,750	3.61	42,400	40,826
7d	12,500	4.44	55,400	55,900
11d	479,000	4.37	2,090,000	2,062,665

TABLE II. THERMODYNAMIC FUNCTIONS OF LITHIUM I.

P (atm.)	T(°K)	α	β	μ	δ	τ	q	Q_{int}	$\frac{-F}{kT}$	$\frac{E}{kT}$	$\frac{S}{k}$	$\frac{C}{k}$
1	5,000	31.87	11.93×10^{-7}	10.18	39.54	110.7	619,100	2.086	0.7351	0.1410	0.8761	0.96936
	10,000	15.94	5.967×10^{-7}	48.16	1994	32,800	2183	4.007	1.388	2.313	3.701	6.8941
	15,000	10.62	3.978×10^{-7}	111.8	6115	16,900	810.5	12.14	2.497	3.252	5.749	2.8744
	20,000	7.698	2.984×10^{-7}	149.7	9250	195,400	675.6	28.94	3.365	3.051	6.416	1.0418
20	5,000	31.87	23.94×10^{-6}	10.08	34.55	41.21	618,700	2.084	0.7344	0.1915	0.9259	0.75353
	10,000	15.94	11.92×10^{-6}	16.22	144.4	657.5	1757	3.224	1.171	1.3195	2.490	3.8226
	15,000	10.62	7.98×10^{-6}	29.80	463.2	2922	432.7	6.484	1.869	2.065	3.934	3.0199
	20,000	7.698	5.96×10^{-6}	41.17	792.7	5753	275.3	11.79	2.468	2.132	4.599	1.3936
100	5,000	31.87	11.93×10^{-5}	10.06	34.31	39.90	618,500	2.084	0.7340	0.2179	0.9520	0.83686
	10,000	15.94	5.967×10^{-5}	14.15	94.46	316.5	1679	3.082	1.125	1.182	2.308	3.0973
	15,000	10.62	3.978×10^{-5}	20.96	211.3	908.8	358.4	5.371	1.681	1.780	3.440	2.4170
	20,000	7.698	2.984×10^{-5}	25.84	300.6	138.2	199.1	8.529	2.143	1.806	3.949	1.4131





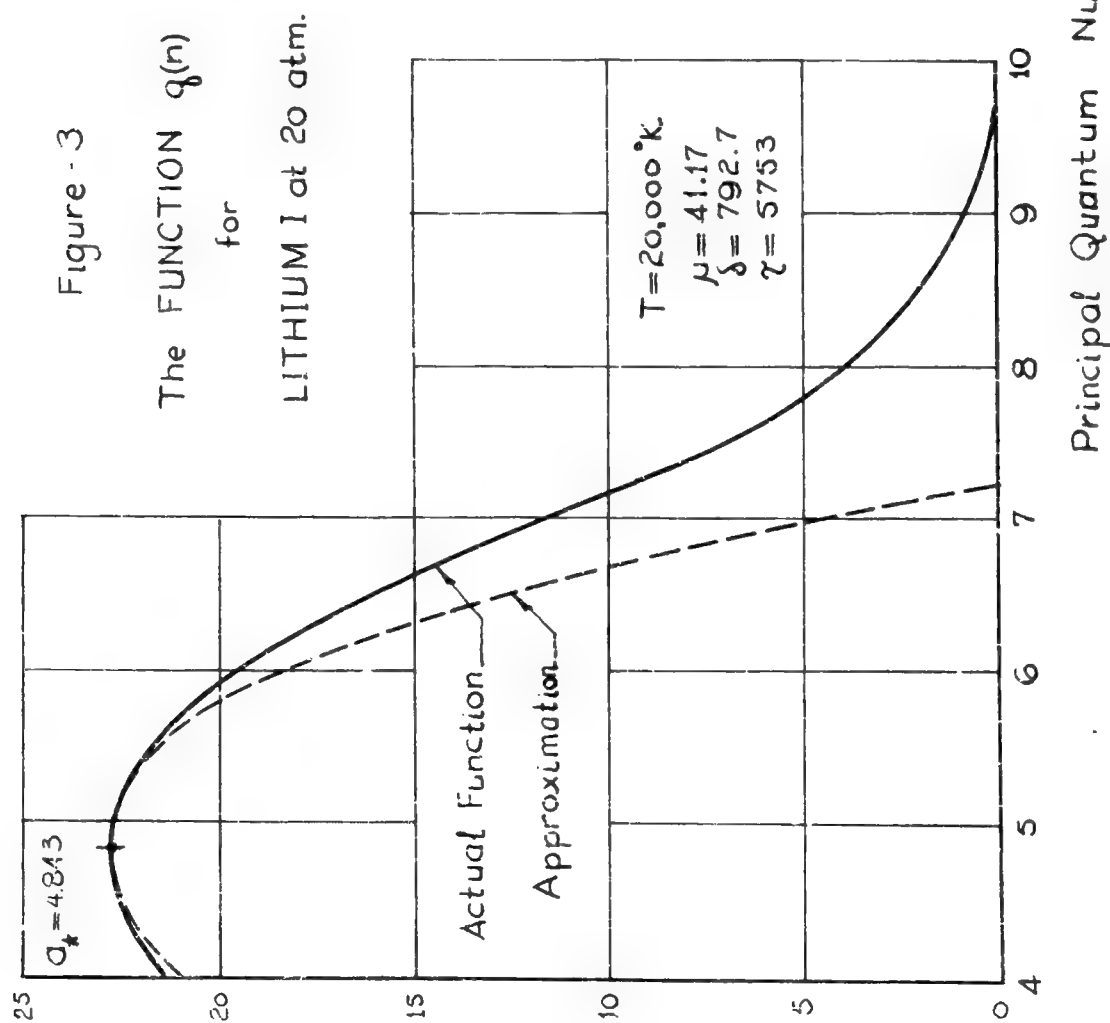
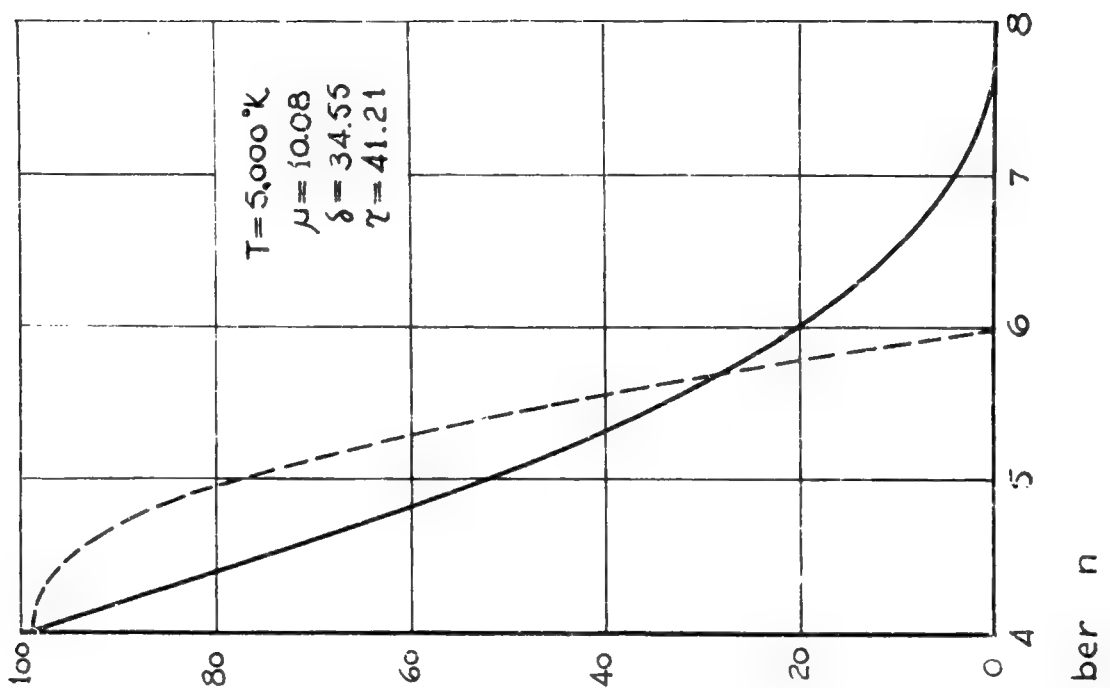
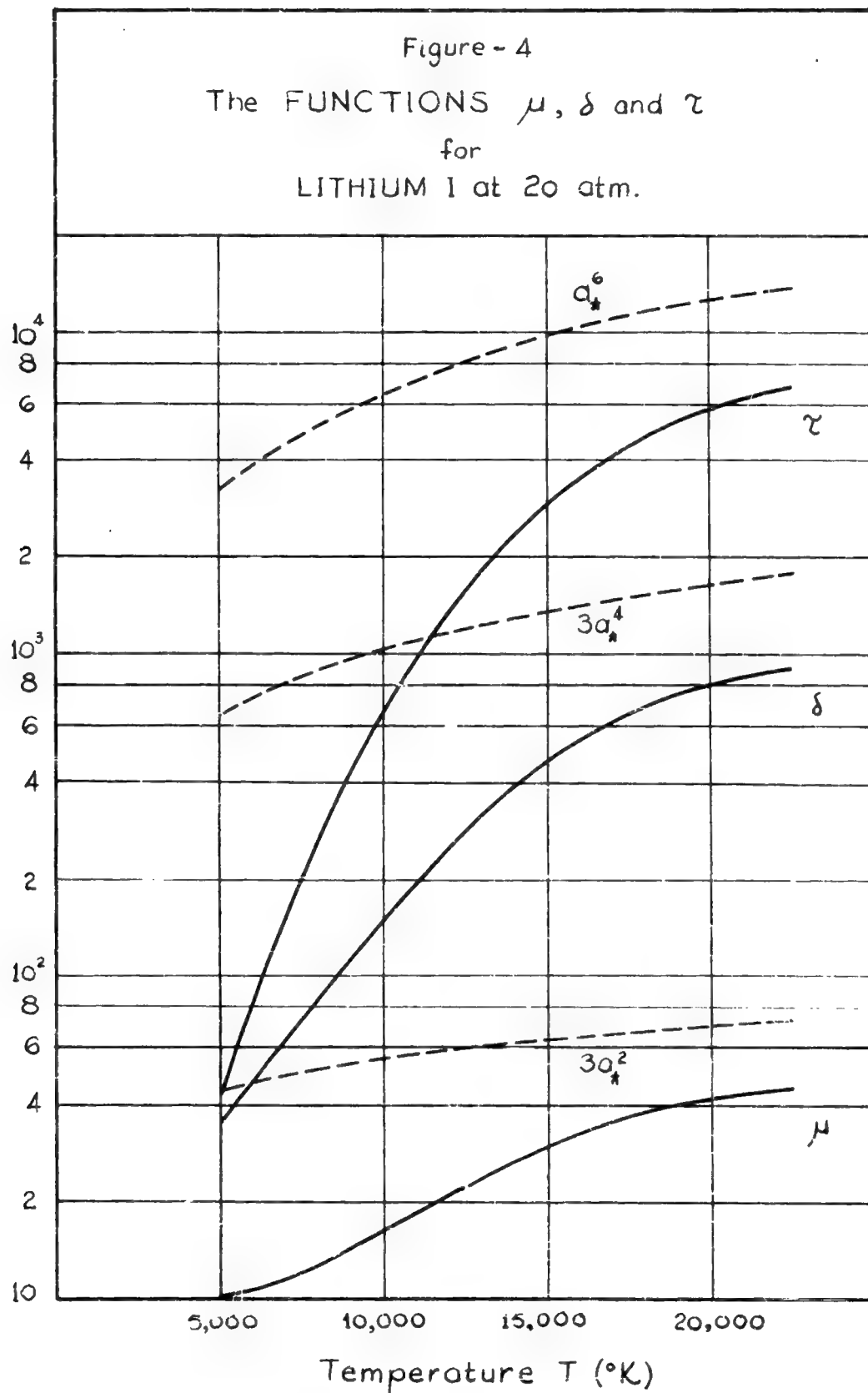
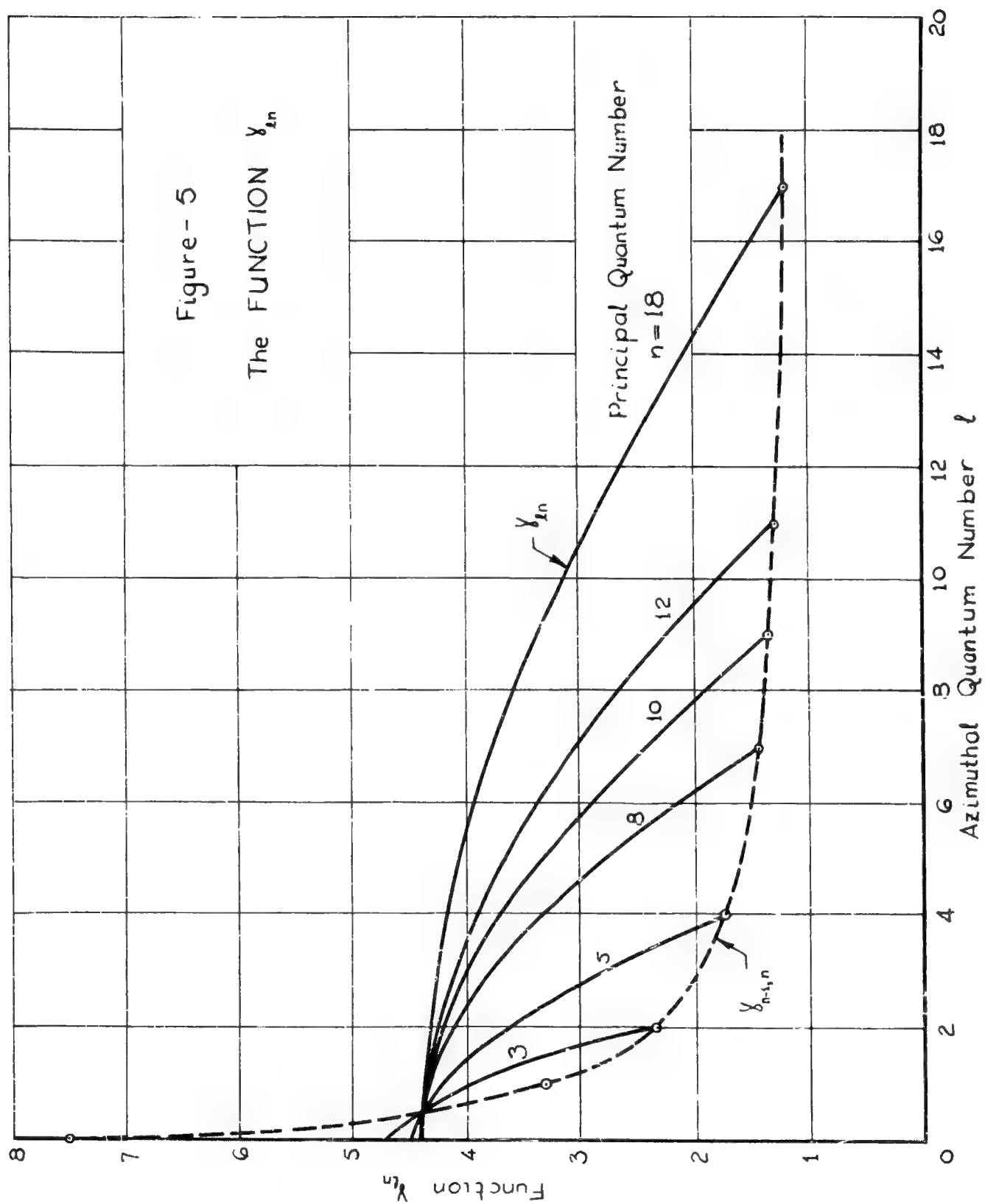
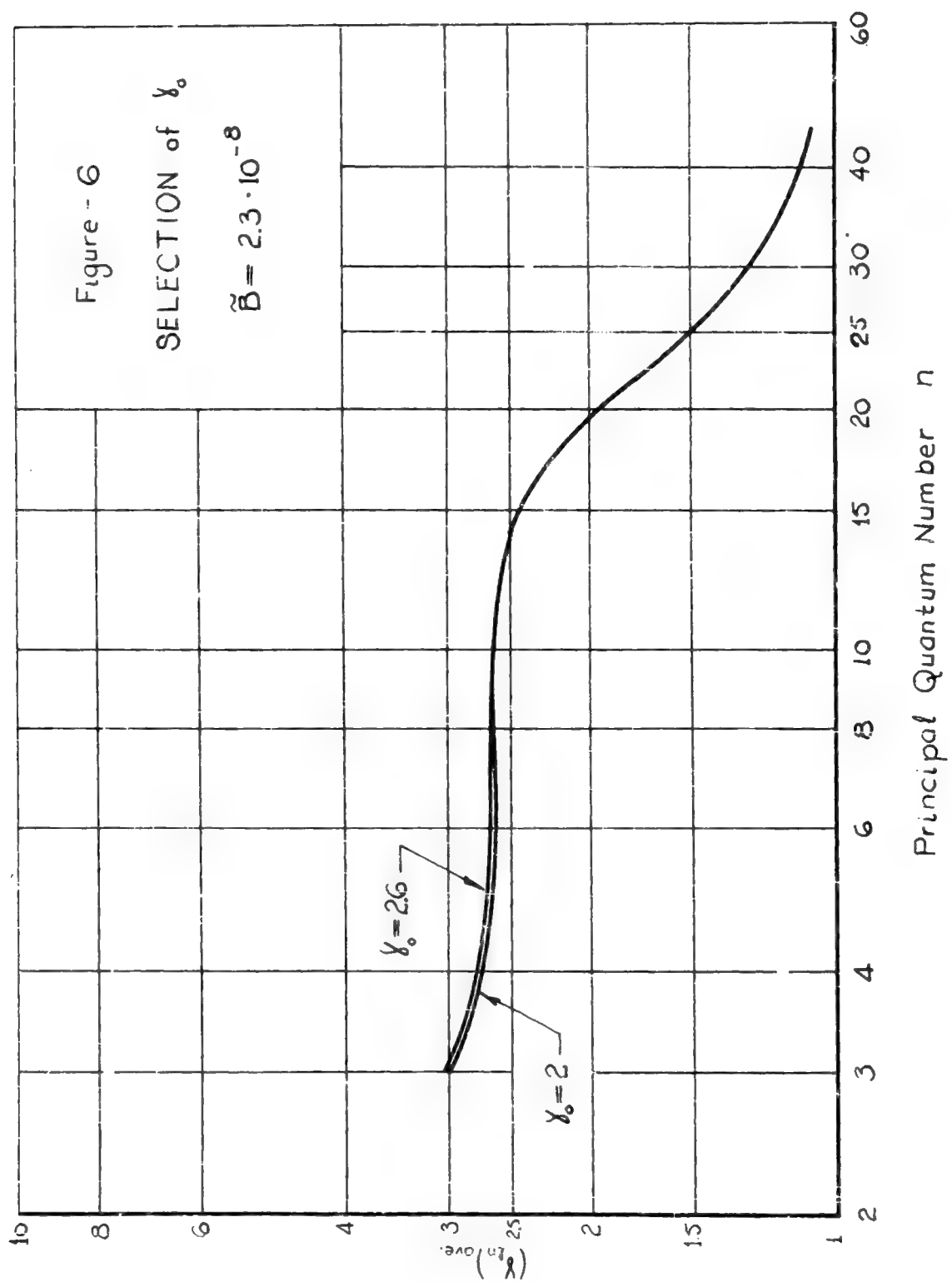
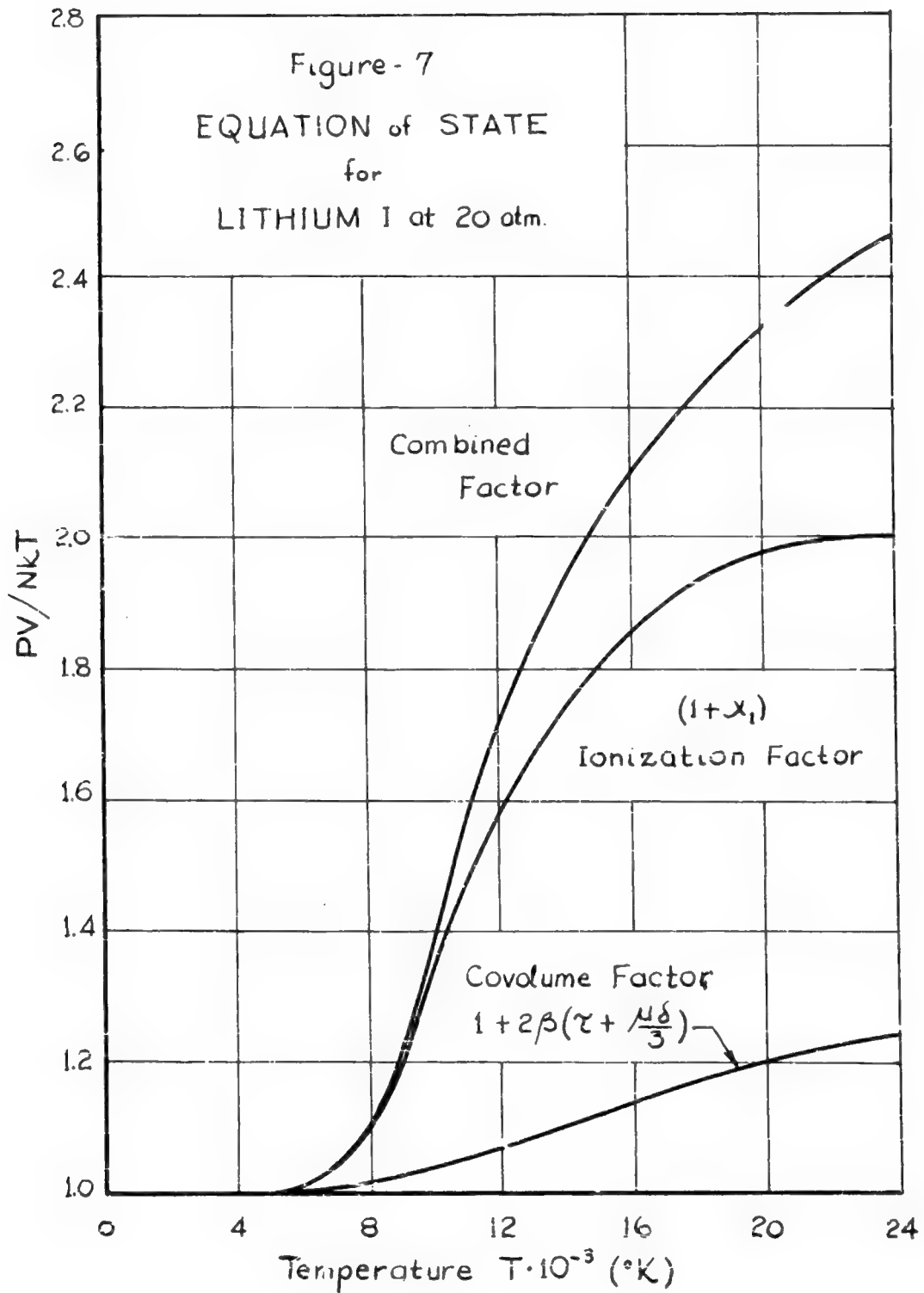


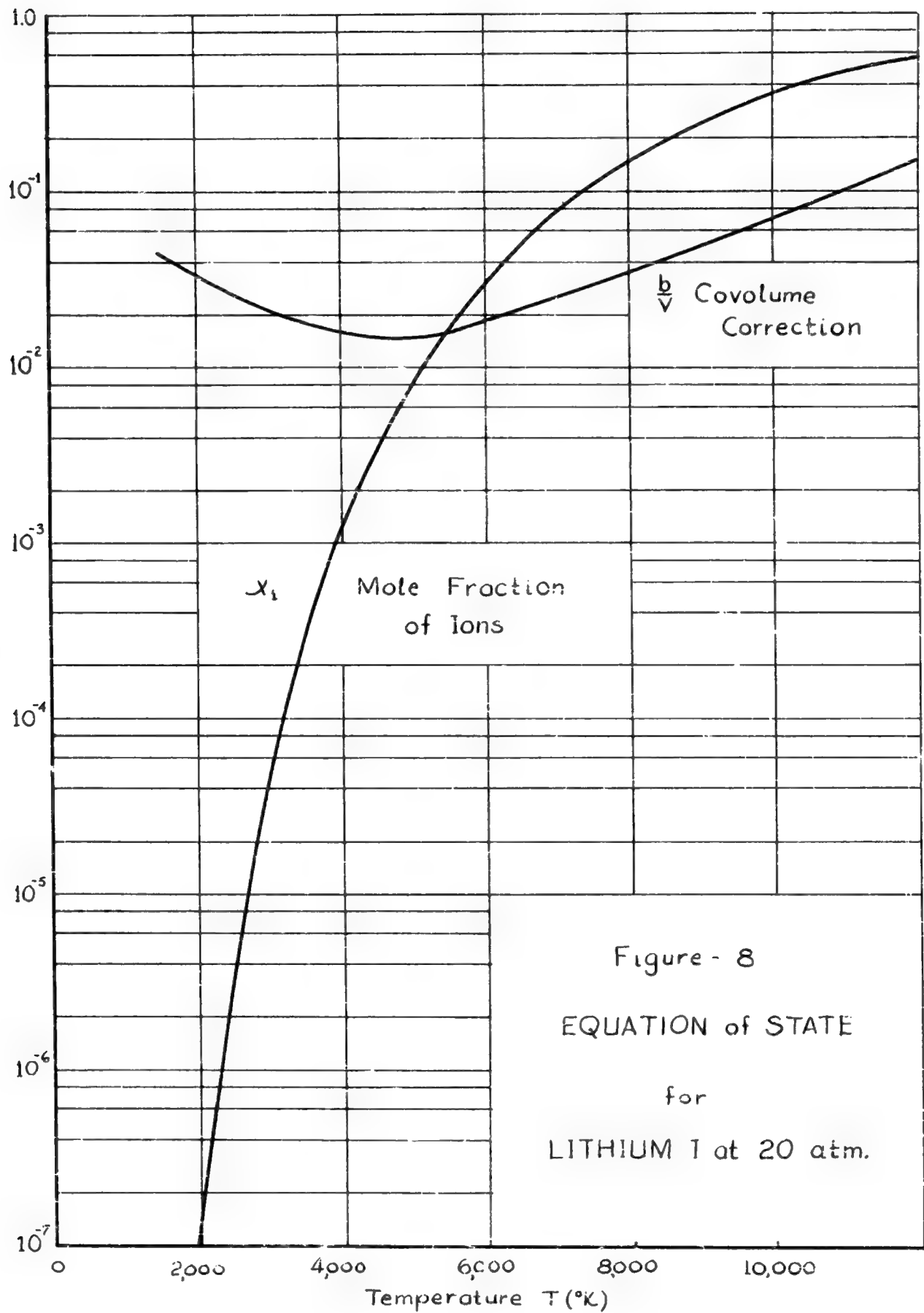
Figure - 3
 The FUNCTION $q(n)$
 for
 LITHIUM I at 20 atm.

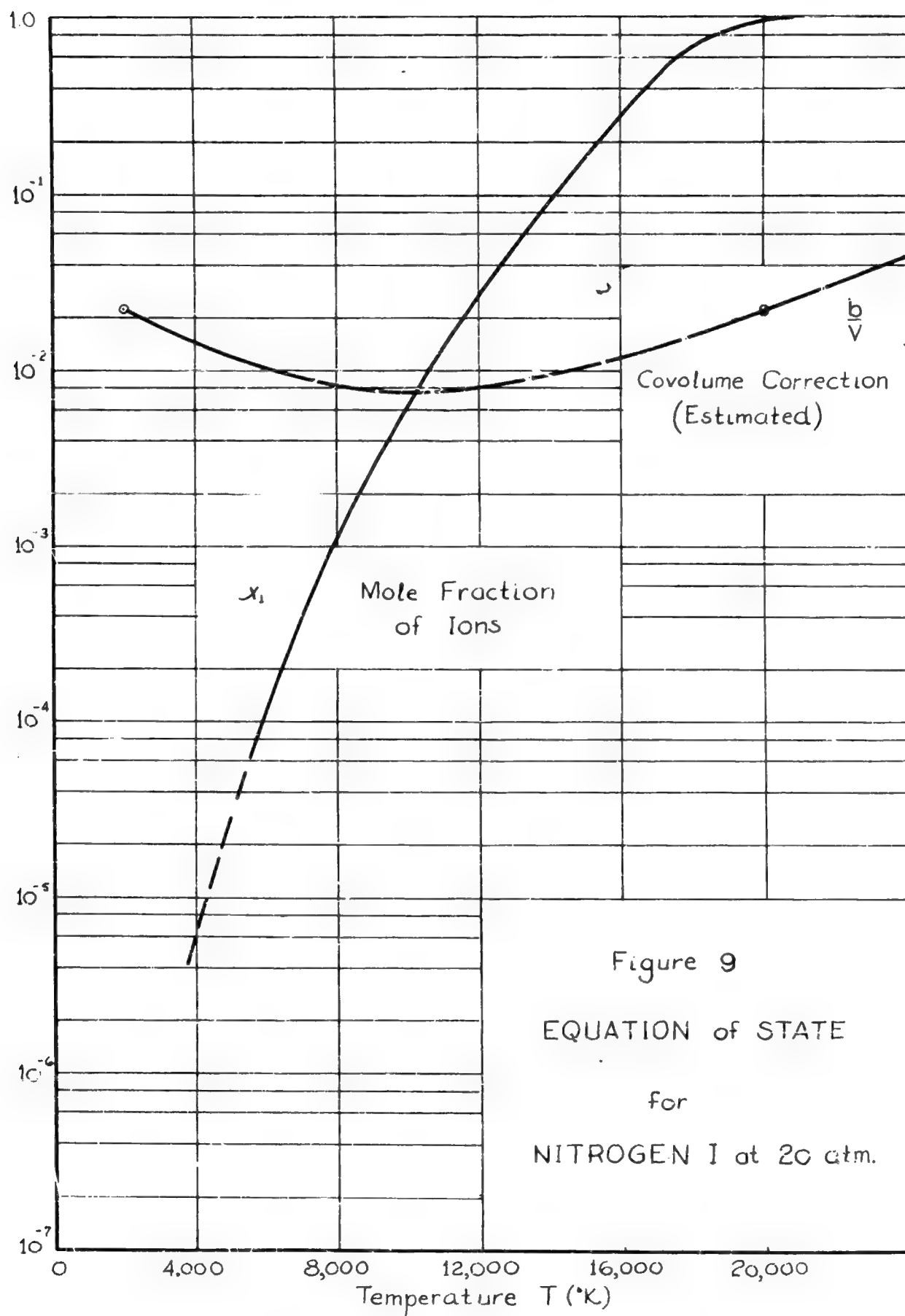


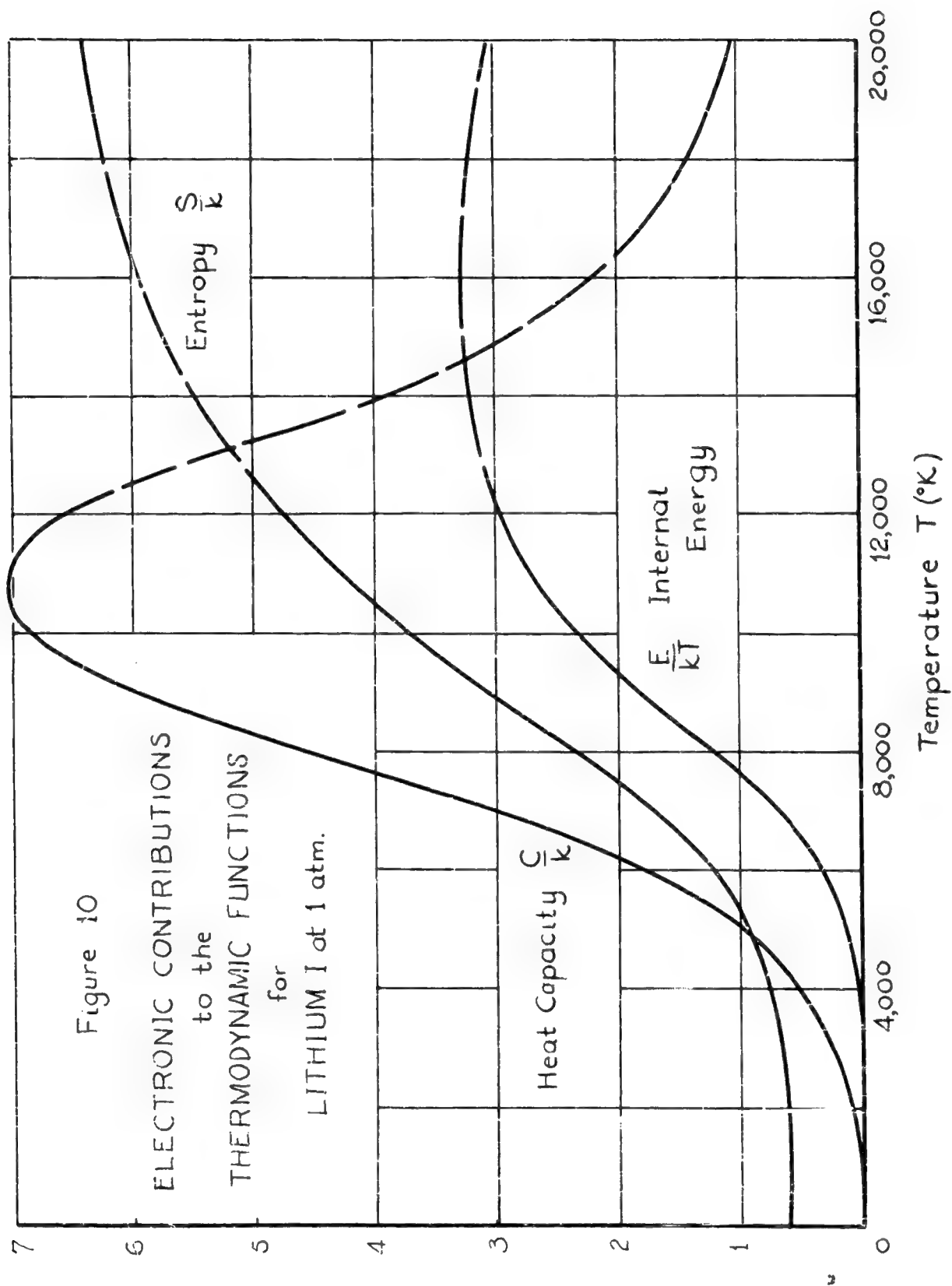












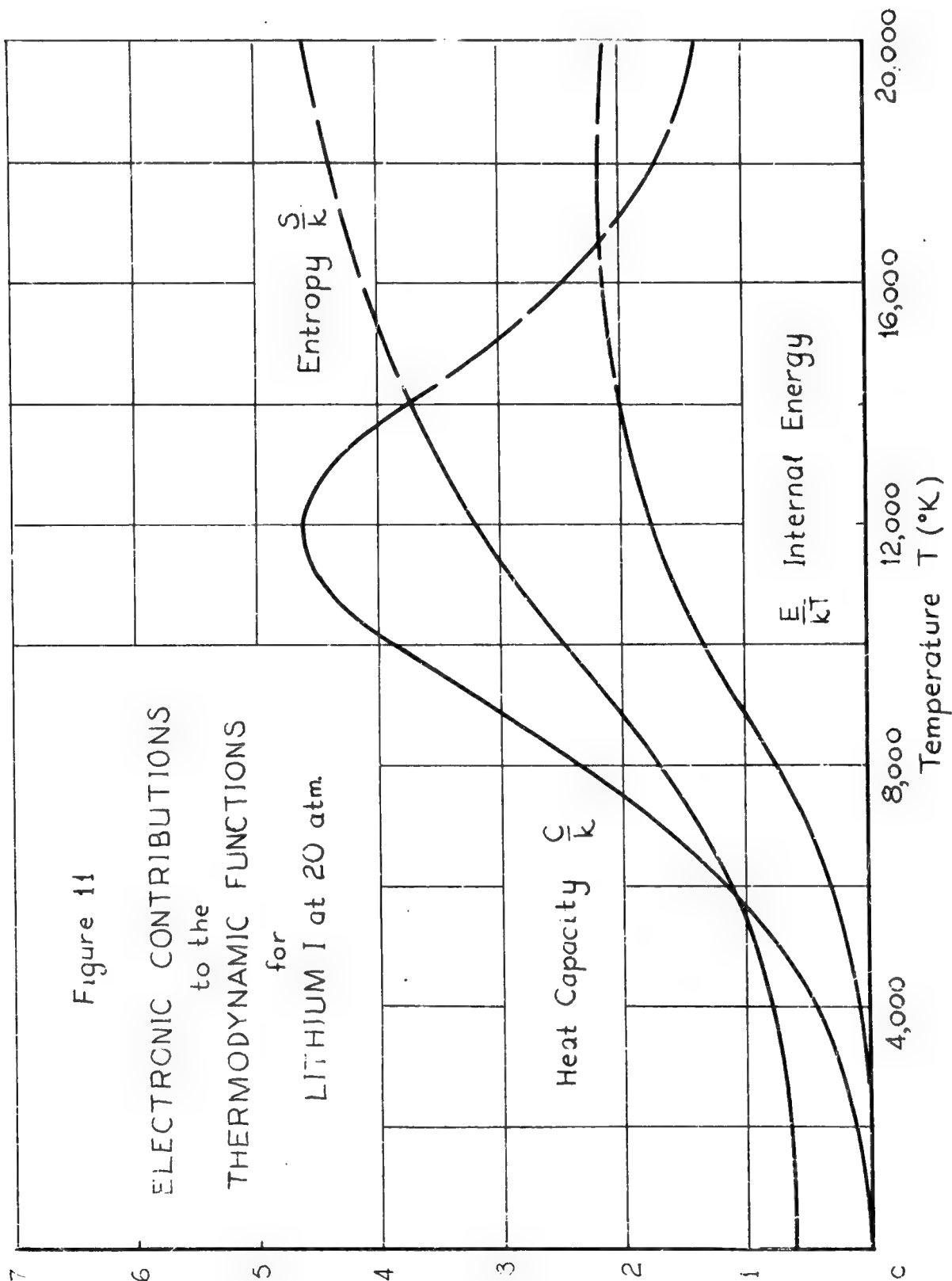
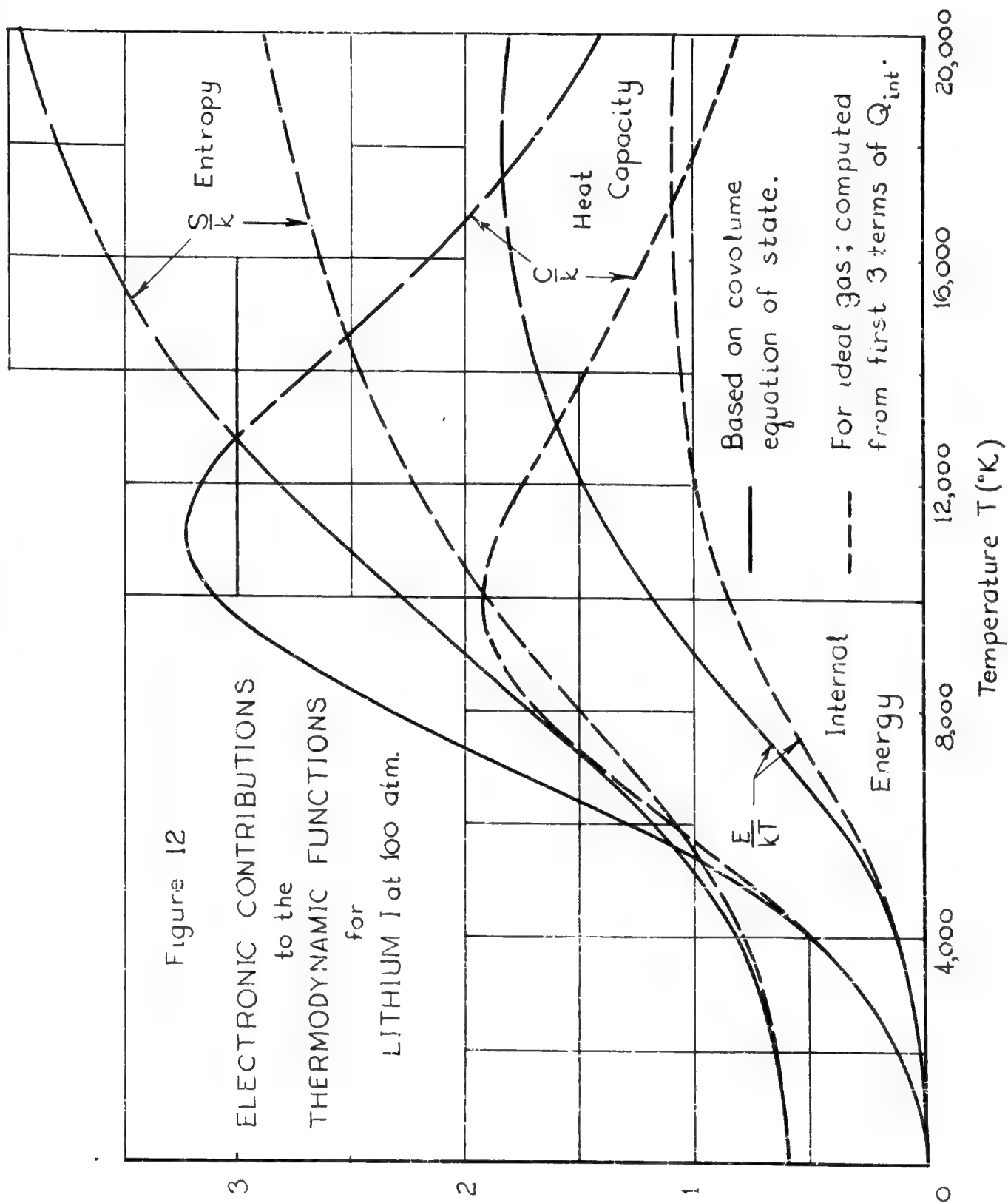


Figure 12
ELECTRONIC CONTRIBUTIONS
to the
THERMODYNAMIC FUNCTIONS
for
LITHIUM I at 100 atm.



APPENDIX A

Classical Solution Thermodynamics

1. The Chemical Potential

For real gases, the fugacity f_i of component i is proportional to the activity λ_i .

$$f_i = \text{const. } \lambda_i \quad (\text{A-1})$$

The activity λ_i , however, is related to the chemical potential μ_i by

$$\lambda_i = e^{\mu_i/kT} \quad (\text{A-2})$$

If we substitute Equation (A-2) in (A-1) and solve for μ_i , we obtain

$$\mu_i = kT \ln\left(\frac{f_i}{\text{const.}}\right)$$

Let the properties of this component in the pure state $()^\circ$ be used as a reference, then

$$\mu_i^\circ = kT \ln\left(\frac{f_i^\circ}{\text{const.}}\right)$$

and it follows that

$$\mu_i = \mu_i^\circ + kT \ln(f_i/f_i^\circ)$$

But the mole fraction N_i/N is given by

$$\frac{N_i}{N} = \frac{f_i}{f_i^\circ}$$

hence:

$$\mu_i = \mu_i^\circ + kT \ln \frac{N_i}{N} \quad (\text{A-3})$$

2. The Entropy

The differential equation defining Gibb's free energy F is

$$dF = -SdT + VdP + \sum_i \mu_i dN_i \quad (\text{A-4})$$

but

$$F = \sum_i \mu_i N_i \quad (\text{A-5})$$

so that

$$dF = \sum_i \mu_i dN_i + \sum_i N_i d\mu_i$$

If we equate this expression to (A-4), we obtain the Gibbs-Duhem relation

$$-SdT + VdP - \sum_i N_i d\mu_i = 0 \quad (\text{A-6})$$

For a constant pressure process $dP=0$ and

$$SdT + \sum_i N_i d\mu_i = 0 \quad (\text{A-7})$$

The entropy may also be defined by Euler's relation for extensive properties

$$S = \sum_i N_i \left(\frac{\partial S}{\partial N_i} \right)_{PTN_j} \quad (\text{A-8})$$

If Equation (A-8) is substituted in (A-7)

$$\sum_i N_i \left\{ \left(\frac{\partial S}{\partial N_i} \right)_{PTN_j} dT + d\mu_i \right\} = 0$$

But N_i is arbitrary, therefore

$$-\left(\frac{\partial \mu_i}{\partial T} \right)_{PN_j} = \left(\frac{\partial S}{\partial N_i} \right)_{PTN_j} \quad (\text{A-9})$$

We can obtain the temperature derivative of μ_i from Equation (A-3)

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P, N_j} = \left(\frac{\partial \mu_i^\circ}{\partial T}\right)_{P, N_j} + k \ln \frac{N_i}{N} \quad (\text{A-10})$$

But for a pure component Equation (A-7) yields

$$\frac{S_i^\circ}{N_i} = -\left(\frac{\partial \mu_i^\circ}{\partial T}\right)_{P, N_j} \quad (\text{A-11})$$

And from (A-9), using (A-10) and (A-11)

$$\left(\frac{\partial S}{\partial N_i}\right)_{P, T, N_j} = \frac{S_i^\circ}{N_i} - k \ln \frac{N_i}{N}$$

the substitution of this expression in Equation (A-8) gives

$$S = \sum_i \left(S_i^\circ - k N_i \ln \frac{N_i}{N} \right) \quad (\text{A-12})$$

3. The Volume

For a constant temperature process, the Gibbs-Duhem relation (A-6) yields

$$V = \sum_i N_i \left(\frac{\partial \mu_i}{\partial P} \right)_T \quad (\text{A-13})$$

The Euler relation for the volume is

$$V = \sum_i N_i \left(\frac{\partial V}{\partial N_i} \right)_{P, T, N_j} \quad (\text{A-14})$$

For a pure component, Equation (A-13) reduces to

$$\frac{V_i^\circ}{N_i} = \left(\frac{\partial \mu_i^\circ}{\partial P} \right)_T \quad (\text{A-15})$$

By using the pressure derivative of μ_i from Equation (A-3) we obtain

$$\left(\frac{\partial \mu_i}{\partial P} \right)_T = \left(\frac{\partial \mu_i^\circ}{\partial P} \right)_T = \frac{V_i^\circ}{N_i} \quad (\text{A-16})$$

where Equation (A-15) has been introduced. The substitution of this expression into Equation (A-13) yields

$$V = \sum_i V_i^\circ \quad (\text{A-17})$$

and

$$\left(\frac{\partial V}{\partial N_i} \right)_{PT, N_j} = \frac{V_i^\circ}{N_i} \quad (\text{A-18})$$

4. The Internal Energy

The Gibbs free energy F may also be defined by

$$F \equiv H - TS = E + PV - TS \quad (\text{A-19})$$

If we introduce Equation (A-5) into this expression and solve for E , the internal energy.

$$E = TS - PV + \sum_i N_i \mu_i \quad (\text{A-20})$$

The application of the relations (A-12) and (A-18) yields

$$E = \sum_i \left\{ T \left(S_i^\circ - k N_i \ln \frac{N_i}{N} \right) - P V_i^\circ + \mu_i N_i \right\}$$

The expression for μ_i from (A-3) may now be introduced

$$E = \sum_i \left\{ TS_i^\circ - PV_i^\circ + N_i \mu_i^\circ \right\}$$

where the quantity in the bracket is evidently the internal energy of the pure component E_i° , hence

$$E = \sum_i E_i^\circ \tag{A-21}$$

APPENDIX B

1. The Associated Laguerre Polynomial

$$L_n^k = \frac{d^k}{dx^k} L_n(x) \quad (B-1)$$

where

$$(1-z)^{-1} \exp\left[\frac{-xz}{1-z}\right] = \sum_{n=0}^{\infty} \frac{L_n(x)}{n!} z \quad (B-2)$$

If Equation (B-2) is differentiated k -times

$$\frac{(-1)^k}{1-z} \exp\left[\frac{-xz}{1-z}\right] \cdot \left[\frac{z}{1-z}\right]^k = \sum_{\lambda=k}^{\infty} \frac{L_{\lambda}^k(x) z^{\lambda}}{\lambda!} \quad (B-3)$$

Define

$$I_{n,m} \equiv \int_0^{\infty} e^{-x} x^{k+p-1} L_n^k(x) L_m^k(x) dx \quad (B-4)$$

where: k, p, n, m are integers

Multiply Equation (B-3) by another Laguerre function evaluated at $z = z_2$

$$\sum_{\lambda, \mu=k}^{\infty} \frac{z_1^{\lambda} z_2^{\mu}}{\lambda! \mu!} L_{\lambda}^k(x) L_{\mu}^k(x) = (z_1 z_2)^k [(1-z_1)(1-z_2)]^{-k-1} \exp\left[-\frac{xz_1}{1-z_1} - \frac{xz_2}{1-z_2}\right]$$

Multiply each side by $e^{-x} x^{k+p-1}$ and integrate

$$\sum_{\lambda, \mu=k}^{\infty} \frac{z_1^{\lambda} z_2^{\mu}}{\lambda! \mu!} I_{\lambda, \mu} = (z_1 z_2)^k [(1-z_1)(1-z_2)]^{-k-1} \int_0^{\infty} x^{k+p-1} \exp\left[-x - \frac{xz_1}{1-z_1} - \frac{xz_2}{1-z_2}\right] dx$$

For $z \geq 0$, this expression readily reduces to

$$\sum_{\lambda, \mu=k}^{\infty} \frac{z_1^\lambda z_2^\mu}{\lambda! \mu!} I_{\lambda, \mu} = \frac{(z_1 z_2)^k [(1-z_1)(1-z_2)]^{p-1} (k+p-1)!}{(1-z_1 z_2)^{k+p}} \quad (B-5)$$

The denominator of Equation (B-5) may be expanded in a Taylor series about the point $z_1 z_2 = 0$

$$(1-z_1 z_2)^{-k-p} = \sum_{\lambda=0}^{\infty} \frac{(k+p+\lambda-1)! (z_1 z_2)^\lambda}{(k+p-1)! \lambda!} \quad (B-6)$$

The term $[(1-z_1)(1-z_2)]^{p-1}$ may also be expanded; thus the expansion of each factor about the point $z=0$ yields

$$[(1-z_1)(1-z_2)]^{p-1} = \sum_{\lambda=0}^{\infty} \frac{(p-1)! (-z_1)^\lambda}{\lambda! (p-1-\lambda)!} \sum_{t=0}^{\infty} \frac{(p-1)! (-z_2)^t}{t! (p-1-t)!} \quad (B-7)$$

The substitution of Equations (B-6, 7) into Equation (B-5) gives

$$\sum_{\lambda, \mu=k}^{\infty} \frac{z_1^\lambda z_2^\mu}{\lambda! \mu!} I_{\lambda, \mu} = \sum_{\lambda, t=0}^{\infty} \sum_{\nu=k}^{\infty} \frac{(-1)^{\lambda+t} (z_1^{\lambda+\nu}) (z_2^{t+\nu}) (p+\nu-1)! [(p-1)!]^2}{\lambda! t! (p-1-\lambda)! (p-1-t)! (\nu-k)!} \quad (B-8)$$

where $\nu \equiv k + \lambda$

An expression for the function $I_{m,m}$ is obtained by setting $\mu = \lambda = m$ and equating the coefficients of the like powers of $(z_1 z_2)$ from the two sides of the above equation. If it is noted that only like values of λ and t yield terms in $(z_1 z_2)^m$, then Equation (B-8) reduces to

$$\begin{aligned}
 \sum_{m=k}^{\infty} \frac{(z_1 z_2)^m I_{m,m}}{(m!)^2} &= \sum_{t=0}^{\infty} \sum_{v=k}^{\infty} \frac{[(p-1)!]^2 (z_1 z_2)^{t+v} (p+v-1)!}{[t!(p-t-1)!]^2 (v-k)!} \\
 &= \sum_{v=k}^{\infty} \frac{[(p-1)!]^2 (p+v-1)!}{(v-k)!} \left\{ \frac{(z_1 z_2)^v}{[(p-1)!]^2} + \right. \\
 &\quad \left. \frac{(z_1 z_2)^{v+1}}{[(p-2)!]^2} + \frac{(z_1 z_2)^{v+2}}{[(p-3)!2!]^2} + \dots + \frac{(z_1 z_2)^{v+p-1}}{[(p-1)!]^2} \right\}
 \end{aligned}$$

Note that the summation over t terminates when $t=p-1$. By equating the coefficients of $(z_1 z_2)$ and using $v^2 + v \equiv m$,

$$I_{m,m} = [m!(p-1)!]^2 \sum_{v=0}^{p-1} \frac{(p+m-1-v)!}{[v!(p-1-v)!]^2 (m-k-v)!} \quad (B-9)$$

The function $I_{m,m}$ for various values of p can be obtained readily.

$$p=1$$

$$I_{m,m} = \frac{(m!)^3}{(m-k)!} \quad (B-10)$$

$$p=2$$

$$I_{m,m} = (m!)^2 \sum_{v=0}^1 \frac{(1+m-v)!}{[(1-v)!v!]^2 (m-v-k)!} = \frac{(m!)^3 (2m-k+1)}{(m-k)!} \quad (B-11)$$

$p=3$

$$I_{m,m} = (m!2!)^2 \sum_{\nu=0}^2 \frac{(m-\nu+2)!}{[(2-\nu)! \nu!]^2 (m-\nu-k)!} \quad (B-12)$$

$$= \frac{(m!)^3}{(m-k)!} (6m^2 - 6mk + k^2 + 6m - 3k + 2)$$

$p=5$

$$I_{m,m} = (m!4!)^2 \sum_{\nu=0}^4 \frac{(m-\nu+4)!}{[(4-\nu)! \nu!]^2 (m-\nu-k)!} \quad (B-13)$$

In the present analysis it will be of interest to define

$$m \equiv n + l$$

$$k \equiv 2l + 1$$

where n and l are the principal and azimuthal quantum numbers respectively. Equation (B-13) yields

$$I_{n+l,n+l} = [(n+l)!4!]^2 \sum_{\nu=0}^4 \frac{(n+l-\nu+4)!}{[(4-\nu)! \nu!]^2 (n+l-\nu-1)!} \quad (B-14)$$

APPENDIX C

The present section summarizes the important relations required for the solution of the simultaneous equations (48) using the approximations (49). The derivatives of q computed from the relation (55) are

$$\begin{aligned}\frac{\partial q}{\partial \mu} &= -\frac{\beta}{1-\beta\tau} \left\{ q^{(2)} + \frac{a^4}{2} q^{(4)} + \epsilon a_*^7 h(a_*) \right\} \\ \frac{\partial q}{\partial \delta} &= -\frac{\beta}{1-\beta\tau} \left\{ q^{(1)} + \frac{a^2}{2} q^{(3)} + \epsilon a_*^5 h(a_*) \right\} \\ \frac{\partial^2 q}{\partial \mu \partial \delta} &= \left(\frac{\beta}{1-\beta\tau} \right)^2 \left\{ q^{(3)} + \frac{a^6}{2} q^{(5)} + \epsilon a_*^9 h(a_*) \right\}\end{aligned}$$

The corresponding derivatives of ϕ , χ and ψ are

$$\begin{aligned}\frac{\partial \phi}{\partial \mu} &= q + \frac{\beta}{1-\beta\tau} \left\{ 3q^{(3)} - \mu q^{(2)} + \frac{a^4}{2} q^{(4)} (3a_*^2 - \mu) + \epsilon a_*^7 h(a_*) (3a_*^2 - \mu) \right\} \\ \frac{\partial \phi}{\partial \delta} &= \frac{\beta}{1-\beta\tau} \left\{ 3q^{(2)} - \mu q^{(1)} + \frac{a^2}{2} q^{(3)} (3a_*^2 - \mu) + \epsilon a_*^5 h(a_*) (3a_*^2 - \mu) \right\} \\ \frac{\partial \phi}{\partial \tau} &= \frac{\beta}{(1-\beta\tau)^2} \left\{ 3[q^{(1)} + \beta(q^{(3)} + \mu q^{(2)} + \delta q^{(2)})] - \mu[q^{(0)} + \beta(q^{(2)} + \mu q^{(1)} + \delta q^{(1)})] \right. \\ &\quad \left. + \frac{q(a)E(a)}{2} (3a_*^2 - \mu) + \epsilon a_*^3 h(a_*) E(a_*) (3a_*^2 - \mu) \right\} \\ \frac{\partial \chi}{\partial \mu} &= \frac{\beta}{1-\beta\tau} \left\{ 3q^{(4)} - \delta q^{(2)} + \frac{a^4}{2} q^{(5)} (3a_*^4 - \delta) + \epsilon a_*^7 h(a_*) (3a_*^4 - \delta) \right\} \\ \frac{\partial \chi}{\partial \delta} &= q + \frac{\beta}{1-\beta\tau} \left\{ 3q^{(3)} - \delta q^{(1)} + \frac{a^2}{2} q^{(4)} (3a_*^4 - \delta) + \epsilon a_*^5 h(a_*) (3a_*^4 - \delta) \right\} \\ \frac{\partial \chi}{\partial \tau} &= \frac{\beta}{(1-\beta\tau)^2} \left\{ 3[q^{(2)} + \beta(q^{(4)} + \mu q^{(3)} + \delta q^{(3)})] - \delta[q^{(0)} + \beta(q^{(2)} + \mu q^{(1)} + \delta q^{(1)})] \right. \\ &\quad \left. + \frac{q(a)E(a)}{2} (3a_*^4 - \delta) + \epsilon a_*^3 h(a_*) E(a_*) (3a_*^4 - \delta) \right\}\end{aligned}$$

$$\begin{aligned}\frac{\partial \psi}{\partial \mu} &= \frac{\beta}{1-\beta\tau} \left\{ q^{(5)} - \tau q^{(4)} + \frac{a^4}{2} q^{(4)} (a^6 - \tau) + \epsilon a^7 h(a_*) (a_*^6 - \tau) \right\} \\ \frac{\partial \psi}{\partial \delta} &= \frac{\beta}{1-\beta\tau} \left\{ q^{(4)} - \tau q^{(3)} + \frac{a^2}{2} q^{(4)} (a^6 - \tau) + \epsilon a^5 h(a_*) (a_*^6 - \tau) \right\} \\ \frac{\partial \psi}{\partial \tau} &= q + \frac{\beta}{(1-\beta\tau)^2} \left\{ q^{(5)} + \beta [q^{(6)} + \mu q^{(5)} + \delta q^{(4)}] - \tau [q^{(6)} + \beta (q^{(3)} + \mu q^{(2)} + \delta q^{(1)})] \right. \\ &\quad \left. + \frac{1}{2} q^{(4)} E(a) (a^6 - \tau) + \epsilon a^3 h(a_*) E(a_*) (a_*^6 - \tau) \right\}\end{aligned}$$

where the function $E(a)$ is defined by

$$E(a) \equiv 1 + \beta (a^6 + \mu a^4 + \delta a^2)$$

In carrying out the actual computations for the three moments by means of the above relations and Equations (48) and (49), a slight simplification can be accomplished by neglecting the weighting function in the lower energy states. This is to say, one can assume an approximation for the sums $q^{(4)}$ (Cf. Equation (57)) which is independent of β . Thus

$$q^{(4)} \equiv \sum_{j=1}^{\lambda} v_j^4 q_j = \sum_{j=1}^{\lambda} v_j^4 g_j e^{W_j/kT - \theta_j} \simeq \sum_{j=1}^{\lambda} v_j^4 g_j e^{W_j/kT}$$

This approximation is especially good for the lower temperature systems ($\beta > 10^{-6}$). However, it is also applicable to the smaller values of β . It is applicable in the first case because the entire weighting function $\simeq 1$. Although this is not the case for $\beta < 10^{-6}$, it may still be used because the contribution to q of the terms $j=1$ to λ is not the major contribution. As previously discussed, the largest contribution stems from the higher energy states. Thus, relatively large errors can be tolerated for the first λ terms of q .